

Oxy-Fuel Gasification in Fluidised Beds

Nicolas Spiegl

Department of Chemical Engineering
Imperial College London of Science, Technology and Medicine

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Abstract

Rising energy demand, up coming shortage of natural gas and oil and increasing awareness of the effect of global warming are the driving forces behind the development of new, highly efficient processes with integrated carbon capture and storage, using fuels with predicted long term availability. Gasification and especially fluidised bed gasification is seen as a promising near zero emissions route to utilise low value coal, waste and biomass for energy production via the integrated gasification combined cycle process (IGCC). The integration of a carbon capture and storage (CCS) technology into the design of IGCC plants changes the design framework for the gasification process as a pure stream of CO₂ at the downstream end of the plant is now available. Therefore a novel oxy-fuel fluidised bed gasification process is proposed in which the gasifier is operated as part of an IGCC plant with pure O₂ and recycled CO₂. Steam is used to enhance the carbon conversion if necessary.

A laboratory scale fluidised bed gasifier capable to operate up to 1000°C and 20 bar was used to study the implications of oxy-fuel firing on flue gas composition and operability of the gasifier. Maintaining a constant feed rate (1 - 6 g/min) a stable fuel gas composition was obtained for up to 30 min. Using a lignite as feedstock, carbon conversions higher than 95% and a fuel gas with a medium heating value were obtained under oxy-fuel conditions. With the addition of steam, the operating temperature could be reduced from 950°C to 850°C while maintaining the gasification performance. The decrease in carbon conversion with increasing pressure was investigated using experimental data from a wire mesh reactor and optical char surface analysis. Strategies to optimize the gasification performance were developed for atmospheric and pressurised operations. Besides the lignite, two bituminous coals and different mixtures of biomass and lignite were tested for their use in an oxy-fuel fluidised bed gasifier. Analysis of the tar, H₂S and NH₃ content of the fuel gas provided information about the influence of operation conditions on the emissions of pollutants.

The results show that oxy-fuel firing of a fluidised bed gasifier could be a promising route to avoid N₂ dilution of the fuel gas and reduce the costs of integrating CCS technology. In order to assist further research, the results obtained in this study are used to derive design recommendations for large scale testing facilities.

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Declaration of Originality

I certify, as the author of this thesis, and as first author of the publications arising, that I was the person primarily involved in the designs, implementation, analysis and manuscript preparation. I declare that the work presented in the thesis is to the best of my knowledge and belief, original except as acknowledged in the text.

Nicolas Spiegl

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Abbreviations & Nomenclature

Abs	Absolute Value
rel	Relative Value
mean	Mean Value
STDEV	Standard Deviation
EM	Electron Microscope
TGA	Thermo Gravimetric Analyser
WMR	Wire Mesh Reactor
FBR	Fluidised Bed Reactor
GL	German Lignite
DM	Daw Mill Coal
PC	Polish Coal
OB	Olive Bagasse
daf	Dry Ash Free
IGCC	Integrated Gasification Combined Cycle
CCS	Carbon Capture and Storage
ASU	Air Separation Unit
CC	Combined Cycle
LHV	Lower Heating Value
HHV	Higher Heating Value
O/C	Oxygen/Fuel-Carbon Ratio on molar basis
CO ₂ /C	Carbon Dioxide/Fuel-Carbon Ratio on molar basis
Steam/CO ₂	Steam/Carbon Dioxide on molar basis
UV-F	Ultra Violet Fluorescence
SEC	Size Exclusion Chromatography
DI	Deionised Water
pf	Pulverised Fuel
F	Volumetric Flow Rate Fuel Gas [l/min], standard conditions
FFR	Fuel Feeding Rate [g/min]
l	Litre (all volumes in this work are given at standard conditions)
bar	as bar gauge
X	Carbon Conversion [%]
x _n	Mole Fraction = Volume Fraction (always assuming ideal gas)
F _n	Volumetric Flow Rate of n [l/min], standard conditions
u _{mf}	Minimum Fluidising Velocity [m/s]
u _s	Superficial Velocity [m/s]
ρ	Density [kg/m ³]
M	Molar Mass [kg/kmol]
d	Particle Diameter [μm]

All gas mixture (example 10% O₂/CO₂) in this work are on v/v basis
Standard Conditions: 20°C and 700mm Hg

1 Introduction

1.1 Background

Gasification and especially Integrated Gasification Combined Cycle (IGCC) technology is seen as a promising option to improve the efficiency of power generation. Advantages include higher efficiencies than conventional coal fired-power plants, lower emissions of greenhouse gases and NO_x and SO_x pollutants, low levels of particulate emissions and market flexibility due to multi product plants [1]. Gasification is an old, but continuously evolving technology [2]. From 1850, gasification of coal produced the ‘town gas’ for light and heat. In the 1940s and 1950s, the development of natural gas supply and transmission replaced the gas-from-coal technology. The supply shortage faced by the Germans in the Second World War led to the development of synthetic fuel from gasification. This technology was later used in South Africa to overcome the lack of crude oil supply. Mainly Sasol, South Africa’s state owned company, in cooperation with Lurgi, a leading German technology supplier in this field, developed the technology further to produce liquid fuels and chemicals from coal rather than from oil. The Arab Oil Embargo of 1973 led to increasing interest in gasification and to the development of the first IGCC power plant. To the present, a number of government agencies in the United States and Europe have provided financial support for IGCC projects to demonstrate feasibility. From 2000 on, commercial developers started operation of IGCC plants without governmental support [3]. A worldwide review at 2007 of gasification technology by the Gasification Technology Council found 417 gasification plants in operation. Coal was used in 55% of them as the main feedstock and 18% were used to generate power [4].

For possible future carbon capture and storage (CCS) oxygen blown gasification may be the most promising route [1]. That is because of two main reasons: (1) The air is separated before the process, avoiding energy and cost intensive processing for downstream CO_2 - N_2 separation (although air separation causes additional costs). (2) Modern gasification processes are already operating under elevated pressure [5] and the trend goes to even higher pressures in the future [6]. This would reduce energy costs for CO_2 compression necessary for CO_2 transportation and storage as a supercritical fluid. The energy demand of CCS technology decreases the overall plant efficiency drastically. The challenge is to improve the plant efficiencies so that the next generations of IGCCs with integrated CCS have the same

efficiency as the top of the range plants today. A large R&D effort is necessary to achieve this.

Advantages in coal conversion and throughput rates make entrained flow gasifiers the preferred option at the moment. However with increasing interest in biomass gasification, waste processing and decentralised small scale applications, fluidised bed gasifiers are becoming interesting again. Fluidised bed gasification on a commercial scale has been used since the original Winkler process was developed [7]. Its advantages are fuel flexibility, load flexibility and ability to process low rank coals, with high ash and sulphur content, making them a promising option for future power generation.

In order to combine the advantages of gasification, fluidised bed operation and oxygen blown processes, a novel process configuration is proposed: Operation of a fluidised bed gasifier with pure O_2 and recycled CO_2 . In combination with an IGCC power plant concept such process has the potential to produce electricity with a high efficiency, based on fuels available in the future, and would produce a stream of pure CO_2 ready for sequestration.

1.2 Objectives

The main objective of the work is to investigate the potential of an oxy-fuel fluidised bed gasification process using a laboratory scale reactor. The project was therefore divided into three steps:

- (1) Modification of an existing laboratory scale fluidised bed reactor to work under oxy-fuel conditions and with continuous fuel feeding.
- (2) Planning and conducting an experimental program to investigate oxy-fuel fluidised bed gasification with the focus on the following key points:
 - Operability of the gasifier under high partial pressure of CO₂
 - Gasification performance under oxy-fuel conditions and effect of operating conditions (different fuels, bed materials, gasification agents, temperatures and pressures)
 - Emission of pollutants (tar, N and S) from a oxy-fuel gasification process
- (3) Using the information to establish the potential of a fluidised bed oxy-fuel gasification process and to give recommendations for the design and operation of a larger scale test facility.

The project was part of the EU Flexgas project founded by the Research Fund for Coal and Steel. The main objective of the project was to promote fluidised bed gasification within industry by overcoming the disadvantages of the process and improve its integration with emerging CCS technology.

1.3 Outline of the Thesis

The literature review in Chapter 2 discusses the motivation behind this work, guides the reader through a step by step development of the proposed oxy-fuel gasification process, provides background information for gasification of solid fuels and reviews the relevant literature.

Chapter 3 describes in detail the construction, modification and operation of the laboratory scale fluidised bed reactor and the analytical procedures. It also provides a detailed analysis of the errors involved.

Chapter 4 – 8 focus on the effect of operating conditions on the gasification performance. The effects of the main operating conditions on the gasification performance under atmospheric pressure are discussed in Chapter 4. Separate pyrolysis and partial combustion experiments are carried out to estimate the contribution to the overall fuel conversion. In addition, experiments are carried out to compare steam and CO₂ as gasification agent. In Chapter 5 the effect of different bed materials and the effect of different bed sizes on the gasification performance are discussed. Comparisons are made between silica sand, char and limestone as bed material. The effect of pressure (range: 5 – 20 bar) on the gasification performance of a German lignite was investigated and the results are summarised in Chapter 6. In the first part of this chapter, the effect of pressure is investigated using data from the fluidised bed reactor, a high pressure wire mesh reactor and optical and electronic microscopy. In the second part, the trends established in the previous chapters are used to develop strategies to optimise the gasification performance under elevated pressure. The gasification performance of different fuel and fuel mixtures is discussed Chapter 7. Two bituminous coals and different mixtures of Olive Bagasse and German lignite are tested as potential fuels for the oxy-fuel fluidised bed gasification process. While the previous chapter focused on the major fuel gas components, in Chapter 8 the effect of operating conditions on the minor fuel gas components (Tar, H₂S and NH₃) is discussed.

The findings of the experimental program are used to derive design recommendations for a large scale fluidised bed testing facility operating under oxy-fuel conditions (Chapter 9).

In Chapter 10, the gas phase equilibrium for a C-H-O system for steam and CO₂ gasification are calculated and compared. In addition the experimental gas compositions from the laboratory scale fluidised bed reactor are compared with equilibrium calculations.

Chapter 11 provides a project summary, the main conclusions obtained in this project are presented and recommendations for further work are given.

2 Literature Review

2.1 Introduction

This chapter provides the background information related to the oxy-fuel gasification concept. It is organised into five sections:

- (1) *Economical, Environmental and Political Background:* The section discusses the motivation behind the project from an economical, environmental and political perspective.
- (2) *Process Background:* The aim of this section is to guide the reader from the basic concept of gasification to the proposed oxy-fuel fluidised bed gasification process. It covers the main types of gasification reactors and their characteristics, a detailed description of the fluidised bed gasification process, an introduction into the IGCC concept, a brief description of the oxy-fuel combustion process and the adoption of the oxy-fuel process for fluidised bed gasification.
- (3) *Aspects of Fuel Processing by Gasification:* This section discusses all aspects of gasification relevant for this work. It includes the steps of gasification, thermodynamics, kinetics, catalytic effect and emissions.
- (4) *Examples of Fluidised Bed Gasification Process:* Selected fluidised bed gasification processes, developed up to pilot and demonstration level, are reviewed to provide a better understanding of the potential and current state of this technology.
- (5) *Summary:* Concluding remarks about the literature available and the position of this project in the wider research field.

2.2 Economical, Environmental and Political Background

To improve the environmental performance of the energy-producing sector, Europe today processes far less coal than 20 years ago. However, recent developments force Europe to rethink: international cooperation leading to agreements like the Kyoto protocol demanding a drastic reduction of CO₂ emissions and the costs of oil and natural gas are rising sharply. Three different approaches to secure an environmentally friendly energy future are being widely discussed: nuclear power, as a replacement for fossil fuels, replacing coal with natural gas and the use of renewable energies. However each technology is facing difficulties. In large parts of Europe, nuclear power is not accepted by the broad population as a replacement for fossil fuels and countries like Germany already agreed to decommission all nuclear power in the near future. The demand for natural gas is likely to increase sharply in the future. As a result prices are expected to rise, making natural gas a very expensive resource. Renewable energy sources like biomass and hydroelectricity are limited in scale while technologies for wind power, tide power and solar power are developing fast but will not be able to replace fossil fuels in the near future, partly because a completely new grid and control infrastructure will be necessary.

A common consensus exists that there will be no single solution to solve the energy problem. Instead a mix of different technologies is seen as the best option for Europe - and coal is playing an important role in that scenario. Coal will be still available in large quantities in the world for the next 200 years [8] and taking into account a constantly rising oil price, mining of European coal may soon be an economic option again. In order to use these coal reserves in an environmentally responsible manner highly efficient coal conversion processes, together with possible carbon capture and storage technologies, have to be developed.

The utilisation of coal results in the emission of a variety of pollutants into the air. These pollutants can be categorised in four main groups: particulate, gases, organics and trace elements. Emissions of particulates were the first to be of concern and to be regulated, because they are very easy to detect and have an immediate impact on people's lives. During the 1960s the emission of sulphur and nitrogen gaseous compounds (SO_x, NO_x from coal combustion, organic sulphur, H₂S, hydrogen

cyanide, ammonia from gasification) became a serious issue. Ten years later organics (POM - polycyclic organic matter) and trace elements have become of concern, mainly because of their possible carcinogenic effects [9]. However the biggest environmental issues today arising from coal are the CO₂ emissions. The extent to which CO₂ emissions from fossil fuel utilisation can be minimised will not only have a big influence on the environment, but it will also determine the future perspectives on commercial applications using coal due to increasing public awareness. Regardless of its environmental impact, coal will continue to play an important role in power generation. It is predicted that coal production will increase by 60% between 2006 and 2030, while proven coal reserves are available in large quantities to meet the rising demand. The increase in coal utilisation will increase the share of coal of total emissions from 42% to 46% [8].

2.3 Process Background

2.3.1 Gasification Processes

2.3.1.1 Introduction into Gasification

Gasification is the thermal conversion of hydrocarbon fuels into a gas mainly consisting of CO, H₂, CO₂ and CH₄. The produced gas (fuel gas) can either be used for synthesis of chemicals, syngas, or for power generation via combustion in a gas turbine. A detailed review of the chemical and physical mechanisms involved in gasification together with a discussion on the available literature is given in section 2.4, page 45.

2.3.1.2 Overview – Different Types of Gasifier

Three main reactor types are used for gasification process: Moving bed (or fixed bed), fluidised bed and entrained flow reactors.

Table 1 shows the main operation conditions and key characteristics of the three different types. The principles of moving bed and entrained flow gasifier are briefly described, while the fluidised bed gasifier, as used in this project, is explained in detail in the next section.

In a moving bed gasifier, the coal is fed counter current or co-current to the gasification agent and moves downwards by gravity. This results in a temperature profile along the bed where coal travels from the coldest point in the reactor to the hottest and is sequentially preheated, dried, de-volatilised, partially combusted and gasified. The main suppliers for this technology are Lurgi GmbH [10] and ENVIROTHERM GmbH [11]. Disadvantages of this type of gasifier include the sensitivity to the amount of fines in the coal and a possible high tar content of the fuel gas. However, the Lurgi fixed bed gasifier has been used since 1955 in South Africa by Sasol on its indirect coal to liquid plants and is up to now the only demonstration of large scale coal gasification with extensive operational experience.

In an entrained flow gasifier, pulverised fuel particles concurrently react with steam and oxygen as oxidant which are fed to the gasifier co-currently via a burner. Using

pure oxygen makes high temperatures possible, which therefore ensure high carbon conversion. Entrained flow gasifiers are characterised by short residence times (several seconds), high carbon conversion (>98%) and tar free product gas. However this type of gasifier requires fuels with a very narrow range of properties regarding for example the ash constituents. Companies offering gasification systems based on that technology include General Electric Energy [12], Royal Dutch Shell plc [13], Siemens AG[14] and Uhde GmbH [15].

Table 1: Important characteristics of the three types of gasifier [16] (modified)

	Moving-bed		Fluid-bed		Entrained-flow
Ash condition	Dry	Slagging	Dry	Agglomeration	Slagging
Preferred coal rank	Low	High	Low	Any	Any
Size [mm]	5-80	5-80	< 5	< 5	0.1
Operation temperature [K]	673-1573	673-1773	1173-1373	1173-1373	1373-1773
Exit gas temperature [K]	Low	Low	Moderate	Moderate	High
Oxidant requirement	Low	Low	Moderate	Moderate	High
Steam requirement	High	Low	Moderate	Moderate	Low
Key characteristics	Hydrocarbon liquids in the raw gas		Large char recycle		Large amount of sensible energy in the hot raw gas
Carbon conversion	> 95%		> 95%	> 95%	> 99%

2.3.1.3 In Detail: The Fluidised Bed Gasifier

In a fluidized bed reactor the gas entering the reactor vessel from the bottom is supporting the bed material in such a way that it becomes fluid-like in nature. The drag and buoyancy force are balancing the gravitational force of the particles. The suspended particles allow a very good gas-solid contact resulting in an almost isothermal bed with very good heat and mass transfer properties [17].

The bed is fluidised by the gasifying agent and the product gas. Air, steam and oxygen are used in various combinations as gasifying agent. It can be differentiated between air blown gasifiers, oxygen enriched air blown gasifiers and oxygen blown gasifiers depending on how the oxidant of the process is provided. Part of the feedstock is directly combusted with the oxygen. The heat of combustion is used to provide the necessary energy for the endothermic gasification reactions. Therefore oxygen demand depends on extent of endothermic gasification reactions, energy required to heat input streams, desired temperature, heating value of the fuel and heat loss of the reactor. Steam is normally added to moderate the temperature and to provide additional gasification agent where necessary. In a fluidised bed system the gas entering the reactor is not only used as a reactant, but also used to fluidise the bed, therefore a relatively large volume is required. In this project CO₂ and in some cases steam will be used to moderate the temperature and fluidise the bed.

The advantages of a fluidised bed reactor are the uniform temperature profile and the high rate of back mixing resulting in an even distribution of the different burn off stages in the bed. To keep the bed in a fluid like state, a certain particle size is required. High temperature can cause ash clinker formation and lead to much larger particles resulting in de-fluidisation. Therefore the bed is kept at a constant temperature well below the initial ash melting temperature [18] by moderating with steam. As a result the operating temperature tends to be less than 1100°C. In order to increase carbon conversion, especially for high ranked coals, higher temperatures would be favourable. One possible approach is to manipulate the feed in order to increase the ash fusion temperature [19] by for example adding acidic components like SiO₂, Al₂O₃ and TiO₂ [20].

Fluidised bed gasifiers normally achieve a lower carbon conversion than entrained flow gasifier. Three main reasons can be found for that: (1) the relatively low operating temperature as mentioned before, (2) the constant generation of ash in the bed requires bed draining to maintain a certain bed height. Because of the very good mixing, periodical/constant draining of part of the bed always means losing unconverted carbon and reducing carbon conversion. (3) Particle carry-over with the hot raw gas stream leaving the reactor. Some coal particles shrink in size during gasification and are entrained with the hot raw gas as it leaves the reactor. The superficial velocity in the reactor is designed to keep the bed fluidised for particles with a certain size range and density. Particles which are significantly lighter are driven out of the reactor. These char particles have to be recovered and recycled to the reactor [21]. A cyclone or even a train of cyclones can be used to separate the particles from the flue gas [7].

Conventional fluidised bed gasifiers are operated under dry ash conditions (operating temperature is lower than the ash softening temperature) resulting in low carbon conversion due to low bed temperatures. Therefore the traditional feedstock is low rank coal with high char reactivity and high volatile content. However some attempts have been made to operate under agglomerating ash conditions and therefore increase the maximum possible operating temperature. Higher operating temperatures make it possible to extend the feedstock to high ranked coal with lower char reactivity. Operating between the ash softening point and ash melting point creates large ash agglomerates which are too heavy to be fluidised and sink to the bottom of the reactor where they can be easily removed. Two technologies were developed incorporating this principle: U-gas technology developed by the Institute of Gas Technology (IGT) and the Kellogg Rust Westinghouse (KRW) process [7]. Other design modifications including processes with higher char recycling rate or subsequent combustion of the char containing ash in a fluidised bed combustor (hybrid systems e.g. Air Blown Gasification Cycle technology - ABGC) have further increased the ability to operate with high ranked coals [5]. It has to be mentioned that a high recycling rate, especially of fines, increases the inert content of the bed and consequently leads to lower cold gas efficiency. Therefore for the processing of high ash coals (about 40%), fines recycling is not recommended [22].

In a fluidised bed reactor the gas enters the reactor through a porous plate at the bottom of the reactor. The solid feed stock is fed separately into the bed from the top or the side. A different design is the spouted bed reactor. It was originally developed as a modification of a fluidised bed to overcome the poor quality of fluidisation encountered with uniformly coarse particles. In a spouted bed, high velocity gas (or liquid) is injected through a centrally located small opening at the base of the vessel. The gas jet causes a stream of particles to rise in a central core of the bed of solids. After reaching somewhat above the bed level, the particles rain back into the bed and slowly travel downwards. A systematic cyclic pattern of solids movement is established [23]. The feedstock enters the reactor together with the gas through the central base cone.

Different dimensions of cone, spout, bed diameter and bed height can result in a bed with the characteristics of a spouted bed in the bottom and a fluidised bed on the top. A jet at the apex of the conical base, through which gas and solids enter the reactor, ensures a rapid mixture of the bed. However the particles are not carried above the bed level. The spout is submerged in the bed. The region above the spout behaves like a bubbling fluidised bed [24]. The laboratory scale reactor used in this project applies this concept.

The ABGC (UK) and the KRW (US) process use the spouted bed design. The shape of the base of the gasifier and the spout velocity are optimized to increase the recirculation from spout material and bed material. This ensures rapid mixing of the devolatilizing (sticky) coal particles with non-sticky char particles, avoiding formation of large coal agglomerates, which would lead to bed de-fluidisation and operational problems [25].

2.3.2 Integrated Gasification Combined Cycle - IGCC

2.3.2.1 Introduction

The process of combined cycle power generation integrates the combustion of a combustible gas in a gas turbine with the subsequent use of the hot flue gas for steam generation and a steam turbine for power generation. While in natural gas-fired combined cycle (NGCC), natural gas is directly combusted in the gas turbine; in an integrated gasification combined cycle (IGCC) the fuel gas is produced by a gasifier and combusted in the gas turbine after raw gas cleaning.

IGCC technology uses coal, biomass, refinery residues and waste as feedstock, which will still be available in large quantities for the foreseeable future. Moreover, IGCC is promising as it can achieve high efficiencies and very low emission levels. Furthermore, the development of multi-feedstock/multi-product systems meets the requirements for market flexibility, security of supply and environmental constraints. Figure 1 shows the flexibility in IGCC technology. Having several products would allow to integrate the production into different market segments, thus multiplying the possibilities for generating profits, while achieving lower production costs. Therefore IGCC offers a route to coal utilisation which will meet the requirements of the future [18, 26].

Carbon capture and storage (CCS) is seen as a possibility for future fossil fuel technology. It requires a concentrated, pressurised stream of CO_2 to be produced, with high process efficiency. IGCC plants, mainly based on high pressure gasification produce a pressurised stream of fuel gas. If N_2 as part of the fluidising gas is avoided (O_2 /steam blown, or O_2 /recycled flue gas blown), several techniques could be applied for CCS: (1) Displacing the water-gas shift equilibrium to produce CO_2 and H_2 and using membrane absorption to separate CO_2 . (2) Burning H_2 and CO separately. (3) Burning the gas with O_2 and CO_2 recycled from the same combustion process in the gas turbine [27, 28].

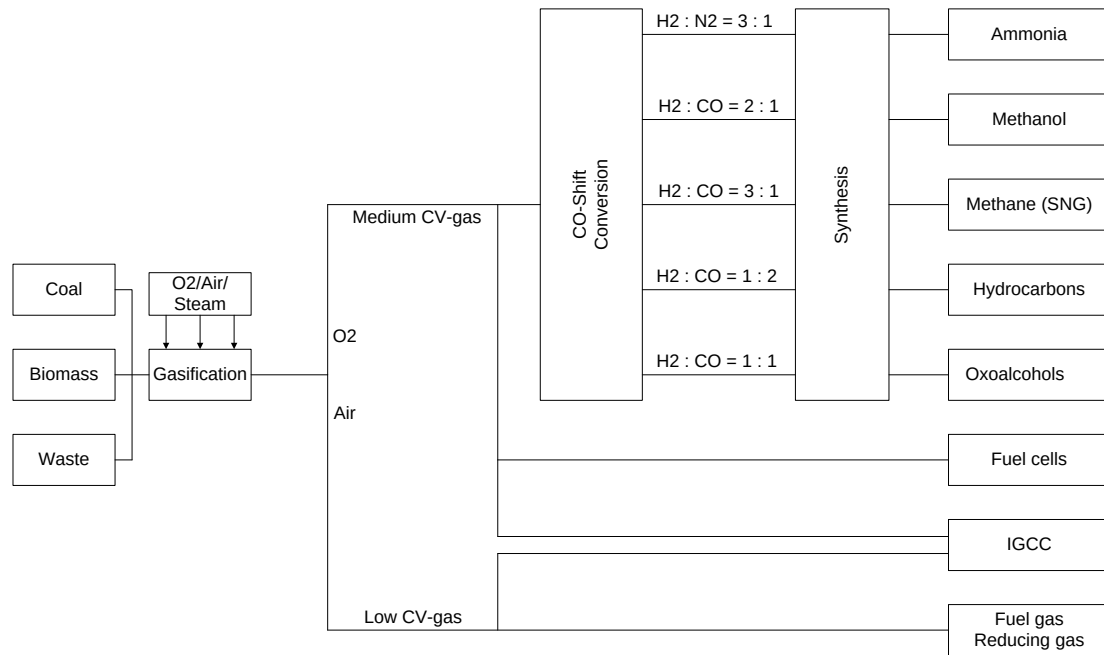


Figure 1: Multi-feedstock/multi-product gasification [5] (modified).

2.3.2.2 IGCC – Plant Layout

An IGCC process consists of a gasification unit, a gas cleaning system, combustion gas turbine and steam generator/turbine. For oxy-fuel or oxygen enriched gasification an additional air separation unit (ASU) is necessary. An highly integrated process design is required to achieve high efficiencies [29]. The gasification unit is the core part of the IGCC plant. It will always be designed for the available feedstock (coal, biomass, pet-coke, waste or co-feeding) and the desired gas utilisation (power generation and or chemical production). Highly flexible processes are certainly most likely to meet the requirements of future challenges.

Figure 2 shows a standard IGCC plant layout and the main material streams between the units. It consists of three main parts: the optional Air Separation Unit, providing oxygen for the gasifier, the Gasification Island with gasifier and gas cleanup plant and the Gas Turbine Combined Cycle with gas turbine, steam generator and steam turbine.

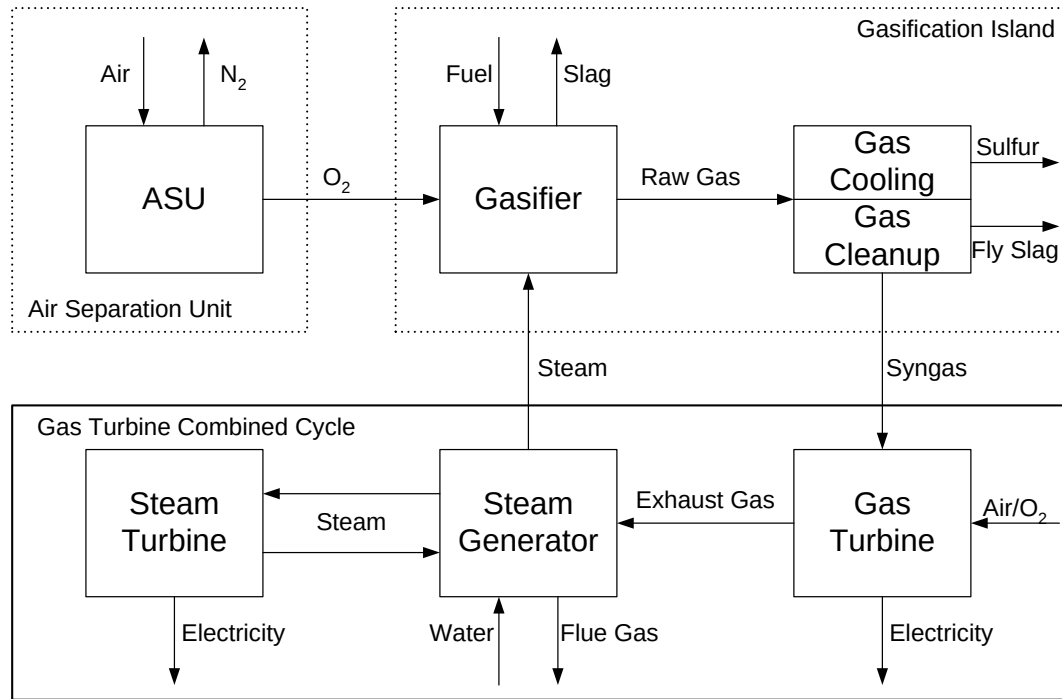


Figure 2: Components of an IGCC plant and main material and energy streams

2.3.2.3 IGCC in the Future

A major effort has to be made to increase the efficiency of fossil fuel based power generation. Increasing the efficiency of a plant will reduce in proportion all emissions to the atmosphere and other waste products simply because less fuel is needed to generate the same amount of electricity. The current trend for coal fired combustion to work with higher steam parameters (super critical and ultra super critical) makes efficiencies of 50+% possible [30]. Combined cycles are another route to high efficiency, because they allow a high temperature gas turbine to be combined with a low temperature final heat utilisation from the steam turbine. Ongoing developments make it possible to burn the hydrogen directly in the gas turbine of a combined cycle with inlet temperatures currently approaching 1400°C [31] (for oxy-fuel gas turbine see below). High inlet temperatures at the gas turbine are the main reason for improving efficiency of combined cycle technologies in the last decades. At the moment, pulverised fuel (pf) combustion is the cheapest option for power generation and natural gas fired combined cycle (NGCC) the most environmentally friendly. Taking into account the possibility of carbon capture and storage (CCS), the feedstock availability in the future and the current technology developments, the IGCC concept can become an economical feasible option for large scale power generation.

Regarding efficiency, supercritical pf combustion and IGCC are equal. Ultra supercritical pf combustion is certainly more efficient than IGCC technology nowadays [32], not including CCS capability. Because of the special advantages, the CCS and IGCC integrated power generation with gasification might be the more efficient and cheaper option.

The future for gasification technology looks bright. It is predicted that in the near future gasification-based technologies using all carbon-based feedstock will penetrate not only the refining and chemical industries but also the electricity production market with pf combustion. Gasification-based processes will be a technology of choice in the future because the advanced version of the technology will have high efficiency along with cost and performance advantages, and will have the adaptability to meet future market requirements for products and use of feedstock [26].

2.3.3 The Oxy Fuel Concept for Pulverised Fuel Combustion

The idea to replace the nitrogen in the air by recycled CO_2 was originally developed for pf combustion to improve the integration with CCS. In this section the pf concept is briefly discussed before the adoption to fluidised bed gasification is described in the next part. Conventional pf coal-fired boilers use air for combustion. The nitrogen (79% v/v) in the air dilutes the CO_2 in the flue gas requiring expensive N_2 - CO_2 separation processes, like amine stripping or calcium looping, before CO_2 can be compressed and stored. Oxy-fuel processes however use a mixture of recycled flue gas and O_2 from an air separation unit (ASU) with purity of typically 95%. As a result they produce a pure stream of CO_2 ready for storage. Recycling flue gas back to the boiler is necessary to control flame temperature and to provide enough gas volume to carry the heat through the boiler. Replacing the N_2 with the recycled flue gas (mainly CO_2) affects several process factors: (1) Similar adiabatic flame temperature under oxy fuel conditions requires 30% O_2 (compared to 21% O_2 under air blown conditions) for a flue gas cycling rate of 60%. (2) The total flue gas volume leaving the cycle is reduced by about 80%. (3) The gas density is increased due to the higher molecular weight of CO_2 ($M_{\text{CO}_2} = 44 \text{ g/mol}$, $M_{\text{N}_2} = 28 \text{ g/mol}$). (4) CO_2 has a higher heat capacity than N_2 . (5) Higher partial pressure of CO_2 increases the concentration of three-atomic gases in the mixture and therefore changes the gas radiative

properties. As a result, it was suggested that the superheated section (section in a boiler where wet steam is converted to dry steam) has to be increased in order to keep the total capacity constant [33] [34].

One of the main disadvantages of oxy-fuel processes is the required ASU unit. Air separation is a very capital and operational cost intensive process. The ASU for the production of oxygen usually accounts for 15% or more of total plant capital cost, while consuming substantial quantities of electricity for air compression. Any technology that can offer a reduction in the cost of oxygen production will have a substantial impact on the overall economics of oxy-fuel processes [35]. Due to the complexity and costs of an air separation unit, oxy-fuel processes will be only used in large coal fired power plants, and for the production of H_2 and chemicals on a large scale [27].

2.3.4 Adoption of the Oxy-Fuel Concept to Fluidised Bed Gasification

As mentioned above, fluidised bed gasifiers are normally either air/steam or oxygen/steam blown depending on the application. For power generation the nitrogen in the fuel gas can be tolerated and air can be used. In the case the fuel gas is converted to syngas, nitrogen dilution has to be avoided and oxygen would be used. If the CO_2 produced by an IGCC plant has to be separated and stored underground the framework for the gasifier design changes drastically. On the one hand, the design has to be optimised in order to reduce the energy penalty of CCS but on the other hand it means that at the downstream end of the plant a stream of pure and compressed CO_2 will be available. From pf combustion it is well known that CO_2 - N_2 separation is very expensive and causes large capital and operational costs. This makes air blown gasification with post combustion CO_2 sequestration not an attractive option. Using air/steam and oxygen/steam blown gasification the following options for an IGCC plant with CO_2 capture are possible:

- (1) *Air/Steam Blown Scenario*: The fuel gas after cleaning consists of CO , CO_2 , H_2 , CH_4 and N_2 . In a shift converter CO is converted to CO_2 producing H_2 via the water-gas shift reaction. CO_2 is subsequently removed by a chemical or physical process. The gas at this point consists of mainly N_2 and H_2 . It could be combusted in a gas turbine leaving only water and N_2 . CH_4 would have to

be removed prior to combustion or its quantity kept at a minimum by the gasification conditions as it would from CO₂ in the gas turbine.

- (2) *Oxygen/Steam Blown Scenario I:* Similar to the previous one except fuel gas for the gas turbine would be almost pure hydrogen. Nitrogen from the ASU unit can be used to operate the gas turbine.
- (3) *Oxygen/Steam Blown Scenario II:* The clean fuel gas would be directly combusted in the gas turbine. The off gas would consist only of CO₂ and water. Water could be condensed and a pure stream of CO₂ would be available for subsequent storage.

Proposed Oxy-Fuel Scenario: If CO₂ is available at the downstream end of the process, steam or nitrogen could be replaced with CO₂ at no extra costs. The fluidised bed reactor would be operated with pure O₂ from an ASU (similar to the oxygen/steam case) and CO₂ recycled from the downstream end of the plant. A schematic diagram of the process configuration is shown in Figure 3. The raw fuel gas is cleaned to a degree where it can be combusted in the gas turbine using again pure O₂ as oxidiser mixed with recycled CO₂. After passing the heat recovery boiler of the combined cycle, the water is condensed and part of the CO₂ is recycled back to the gasifier while the rest is ready for storage. Compared to Scenario I and II, no shift converter and no CO₂ removal would be necessary. Compared to scenario III, no steam would have to be produced. Steam for a gasification plant is either produced by heat integration of the plant or by an auxiliary boiler. For an oxy-fuel fluidised bed gasifier, no boiler would be necessary and all the steam raised by process heat could be used in the heat recovery boiler in the combined cycle to produce electricity. In some case it could be desirable to replace some of the CO₂ going into the gasifier with steam in order to increase carbon conversion or increase the H₂/CO ratio of the fuel gas. But significantly less steam than in the oxygen/steam blown case would be required.

As in the case of oxy-fuel processing, operating the gasifier with a high partial pressure of CO₂ affects virtually all aspects of the process: (1) CO₂ as fluidising agent and temperature moderator: The different density and thermal properties compared to

N_2 and steam would require a totally new configuration for the process. For example, similar to oxy-fuel pf-combustion, a higher oxygen to fuel ratio would be probably necessary to archive similar temperatures. Furthermore, CO_2 is known to affect the swelling and agglomeration properties of coal [36]. For a fluidised bed reactor these are key parameters as they influence the fluidising behaviour of the reactor. (2) CO_2 as main gasification agent: The char-steam reaction is obviously different from the char- CO_2 reaction. A detailed analysis of this is given in the next section and it is also part of the experimental program in this project as is the operability of the gasifier (4.5, page 128). (3) Combustion of a CO_2 rich gas in the gas turbine: Gas turbine development so far was focused on increasing the maximum temperature in order to combust gases high in H_2 . Considering the differences in the thermal properties (higher specific heat and lower density of the working fluid,) either existing gas turbines need to be modified [37] or even the development of new turbines will be required [38].

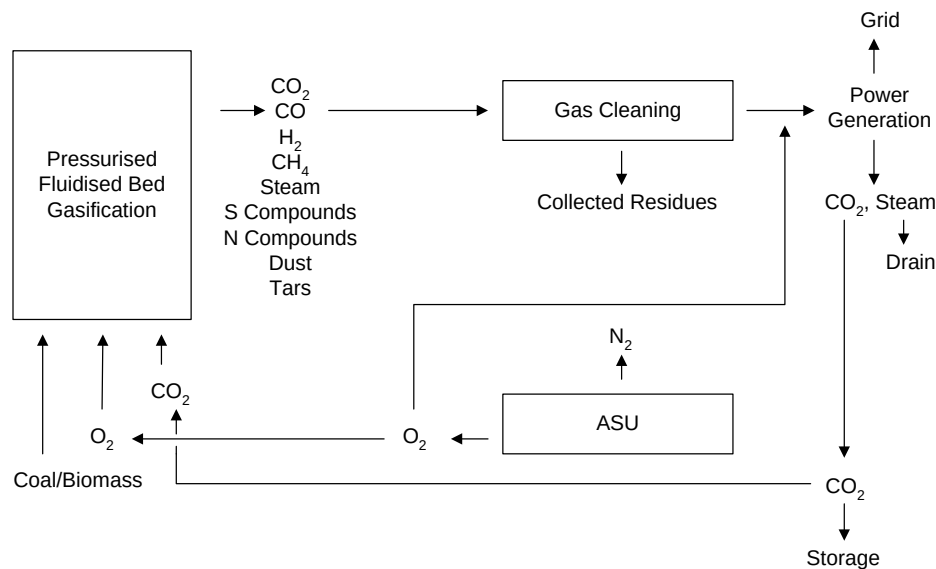


Figure 3: Basic flow sheet of an IGCC power plant with integrated carbon capture and storage based on oxygen blown fluidised bed reactor with flue gas recycling loop.

2.3.5 Gasification process with recycled CO₂

The actual use of recycled CO₂ in large scale gasification processes is not very common. It is occasionally used to replace nitrogen for pneumatic fuel transportation - especially when it is desirable to avoid nitrogen contamination of the syngas [7]. More frequently, recycled CO₂ is used in syngas production by reforming to adjust the CO/H₂ ratio [39]. The concept of operating a fluidised bed gasifier with pure O₂ and recycled CO₂ is a novel process configuration. Nevertheless, using recycled CO₂ for different purposes was considered by a number of authors proposing new process options. This section gives an overview of the proposed concepts.

- (1) Romano et al. [40, 41] used thermodynamic equilibrium calculations to assess the performance of three novel plant configurations for near-zero emissions power generation from coal. One of the plants consists of an entrained flow gasifier operating at 70 bar. The gasifier is O₂/steam blown and recycled CO₂ is used to replace N₂ for dry fuel feeding. The fuel gas stream is cooled to 850°C in a syngas cooler, cleaned via hot gas particle cleaning technology and combusted in a gas turbine using pure O₂ and recycled CO₂. The technology required for the hot fuel gas cleaning process and the development of a gas turbine operating with CO₂ based stream is seen as the main obstacle for the development of such a process. The overall electrical efficiency of the plant was calculated to be around 45% (LHV) including carbon capture and storage.
- (2) Jillon et al. [42] proposed an IGCC plant with two CO₂ recycle streams. In the model, the first stream is used to control the fuel gas composition in a Conocophillips type of gasifier by injecting recycled CO₂ together with the oxygen into the gasifier. The second CO₂ stream is used to replace N₂ as temperature moderator in the gas turbine. Only a simplified model of the gasification process is used to simulate the effect of operating conditions on gasification performance. Two effects of the recycled CO₂ on the gasification performance are shown by the used CFD model: (1) change in temperature profile as the rate of the endothermic CO₂ gasification of coal is increased by increasing CO₂ recycling rate and (2) possible control of the syngas

composition with the CO₂ recycling rate. No information is given whether a real gas turbine was used as a basis for the model. The emphasis of the work is on process control and therefore no further information about the feasibility of the project or possible technical and financial challenges are given.

- (3) Andries et al. [43] reported about plans to modify a pressurised fluidised bed reactor with 1.6 MW thermal capacity for oxy-fuel gasification and combustion with flue gas recycling. The fluidised bed is connected to a combustor where flue gas can be combusted with additional oxygen. The objective of the project was to study the effect of operational parameters on flue gas composition, conversion, in-situ sulphur removal and formation of nitrogen compounds. A second paper published by the same group [44] reports primary results of oxy-fuel fluidised bed combustion at 850°C with 24% and 27% O₂. No results were published on the oxy-fuel gasification concept. The preliminary findings presented in the combustion paper can be summarised as follows: (1) no influence of recycled NO on overall NO emission (2) NO is determined by the level of oxygen at the outlet and the fuel-N input. (3) Oxygen level at the input seems to have no influence on the NO emission (4) NO emissions are not influenced by replacing N₂ with CO₂.
- (4) Lath et al. [45] proposed a new process for the production of CO. The key component would be a slagging fixed bed gasifier. The gasifier would be oxygen blown and CO₂ used as a temperature moderator. The proposed process would operate under slightly elevated pressure and would produce a flue gas high in CO (90 - 92%). Furthermore it is claimed that running a gasifier under such conditions is economical proven.
- (5) Shao et al. [46] described a study of a power plant concept based on a combined cycle powered either by natural gas or fuel gas from a gasifier. In the gasifier, pure oxygen and steam is used as gasification agent. The gas turbine is operated with pure O₂ and recycled CO₂ to improve the integration with CCS. The main focus of the paper is the possible integration of the air separation unit with the CO₂ capture unit. The problem to operate a gas turbine

with a CO₂ based stream is not addressed in this report. The performance of the gasifier is calculated based on thermodynamic equilibrium calculations.

- (6) Normann et al. [47] proposed an oxy-fuel process where fuel would be burned in a slightly sub stoichiometric ratio. Producing heat and additional flue gas for subsequent chemical synthesis (dimethyl ether production) would reduce the production cost for air separation. The process includes co-processing of up to 20% biomass. The study is based on an Aspen Plus simulation. The key issue identified is the oxygen lean combustion or gasification and the related issues in coal conversion and high temperature corrosion.

From these references two driving forces behind the development of gasification processes with CO₂ recycle can be identified: (1) production of pure CO and (2) increasing plant efficiency by using the CO₂ available from the CCS integration. The second reason is certainly the dominating one. It also seems that the majority of the studies are of theoretical nature and are not addressing issues arising from the high partial pressure of CO₂ in the gasifier.

2.4 Aspects of Fuel Processing by Gasification

2.4.1 Introduction

Gasification involves several steps: pyrolysis during which volatile matter is evolved and tars, oils, phenols and hydrocarbon gases are formed, the homogeneous reaction of gaseous pyrolysis products and the gasification of the organic solid residues which become relevant when the temperature exceeds approximately 700°C [5, 48]. In auto-thermal combustion the reaction of the solid residues and the gaseous products with oxygen provide the necessary heat. These steps in the gasification process are similar for the full range of potential feedstock. This justifies the common approach to concentrate on the ‘simple’ gasification of pure carbon and discuss the specific feed characteristics separately [7].

2.4.2 Pyrolysis

When fossil fuels are heated up they divide into a volatile, hydrogen rich, fraction (gases and tar) and a carbon-rich, solid fraction (char). This process is called pyrolysis. Pyrolysis can be divided into primary pyrolysis, where mostly tar is released and secondary pyrolysis, where HCN, CO and H₂ are released and the primary pyrolysis products take part in secondary reactions. As temperature increases three processes occur in the temperature range of 473-673 K prior to the actual pyrolysis: (1) breaking of hydrogen bonds, (2) vaporisation and transport of non-covalently bonded molecular phase and (3) low temperature crosslinking in coal with more than 10% oxygen. During primary pyrolysis, the weakest bridges can break producing molecular fragments. These fragments will either be released as tar if they are small enough to vaporise or undergo secondary reactions. The other event occurring in that phase is the decomposition of functional groups and the subsequent release of gases (CO₂, light aliphatics, CH₄, H₂). The end of primary pyrolysis occurs when the release of hydrogen from the hydroaromatics or aliphatic portion of the coal comes to an end. During secondary pyrolysis there is additional methane evolution (from methyl groups), HCN from ring nitrogen compounds, CO from ether links, and H₂ from ring condensations [5].

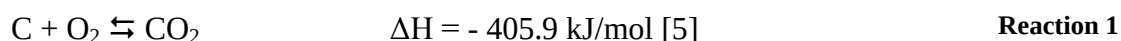
The process of pyrolysis accounts for up to 50% of the heating value produced by coal [49]. Maximisation of the amount of volatiles released during pyrolysis would

therefore reduce the reliance on the slower heterogeneous gas-solid reactions [50]. One way to increase the amounts of volatiles is to increase the speed of the pyrolysis process by increasing the heating rate because rapid pyrolysis results in less char compared to slow pyrolysis [51]. In addition, the pyrolysis process controls a number of feedstock properties with fundamental influence on the gasifier operation (coal swelling, particle agglomeration) and performance (char reactivity, physical structure of char) [49].

2.4.3 Gasification Reactions and Thermodynamic Trends

The gasification reaction of char with different gasification agents (gas-solid reactions) can be summarised in five basic chemical reactions:

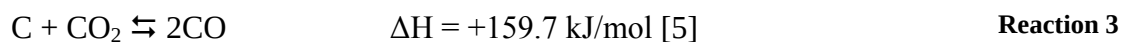
Gasification with oxygen – complete combustion



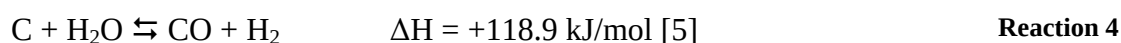
Gasification with oxygen – partial combustion



Gasification with carbon dioxide – Boudouard reaction



Gasification with steam – water-gas reaction

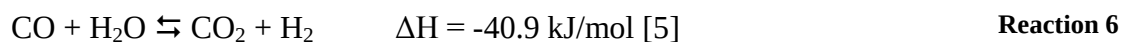


Gasification with hydrogen – hydrogasification reaction

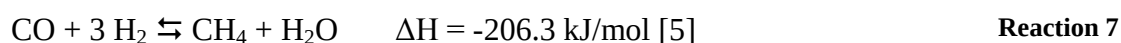


Two gas-phase reactions between the main gaseous products from pyrolysis and char gasification and the gasification agents are important for the final gas composition:

Water-gas shift reaction



Methanation



In addition, free oxygen can react with the gasification products producing heat and influencing the final gas composition. Gasifiers operate under reducing conditions,

therefore the oxygen reacts immediately around the gas nozzles and there is no free oxygen in the rest of the reactor. These seven gasification reactions give the stoichiometry and energy change of the overall process. Due to the spatial distribution of temperature, pressure and concentration in a gasifier, it is not possible to simply combine all the equations and the corresponding equilibria to predict the gas composition of a gasification process. In addition, the kinetics of gas-solid reactions and the pyrolysis reactions during gasification depend on the nature and type of fuel and are subject of ongoing research. Table 2 shows the influence of elevated pressure and temperature on the equilibrium composition of the gas phase [5]. It can be seen that increasing the gasification temperature has an overall desired effect on the process as the concentrations of CO and H₂ increase. Increasing the pressure on the other hand decreases concentrations of CO and H₂. In the case of CH₄ its concentration in the fuel gas increases with increasing pressure: For power generation and production of synthetic natural gas high levels of CH₄ are an advantage while for syngas and hydrogen production it is not desired. However, almost all commercial processes for coal gasification operate under elevated pressure. This is due to reduced equipment size and efficiency advantages in gas compression for downstream processing. Increasing pressure in a bubbling fluidised bed reactor leads to relatively smaller bubbles and therefore higher performance of pressurised compared to atmospheric fluidised bed gasification processes [52].

Table 2: The equilibrium trends for the C-H-O systems [5]

	Temperature ↑	Pressure ↑
H ₂ O	↓	↑
H ₂	↑	↓
CO	↑	↓
CO ₂	↓	→
CH ₄	↓	↑

2.4.4 Gas-Solid Reactions

2.4.4.1 Introduction

As the gas solid reaction of gasification agent and char is the slowest step, it will govern the overall reaction rate [7]. It is necessary to distinguish between the chemical and physical mechanisms involved in the overall process and establish which controls the measurable rate of reaction, i.e. the effective reactivity. This is shown in Figure 4. On the left hand side the rate controlling step in the different temperature zones is shown: I – reaction rate controlled, II – pore diffusion controlled and III – film/bulk diffusion controlled. On the right hand side the rate controlling step for the gasification reactions at different temperatures is shown. It can be seen that fluidised bed gasification, which is carried out in the temperature range from 700°C to 1100°C is in the region where both the chemical reaction and mass transfer influence the rate of reaction.

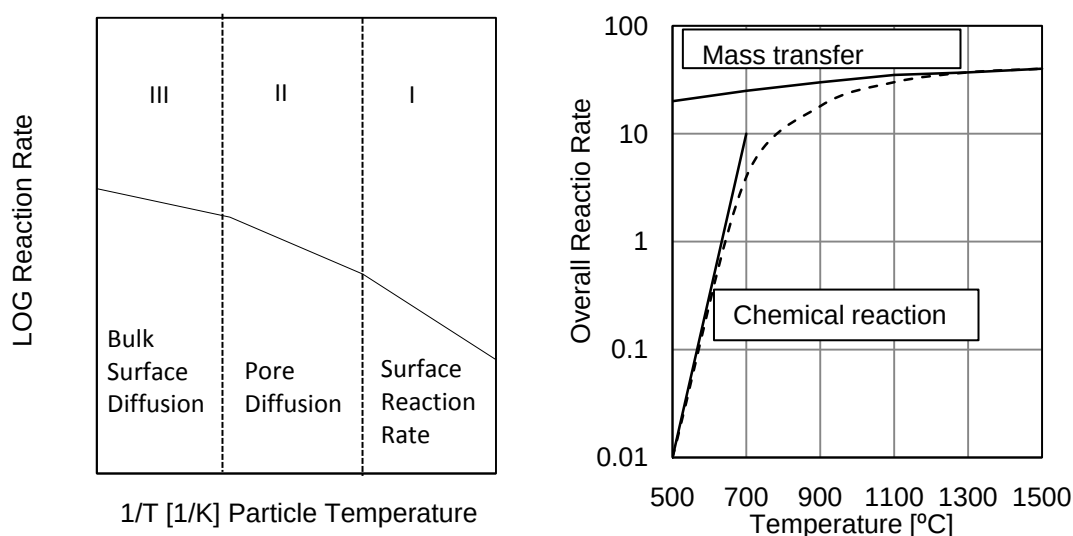


Figure 4: Left – Effective reaction rates in temperature zones. Right – Overall reaction rates as function of temperature. (Graphic adopted from Higman et al. [7])

Care has to be taken to differentiate between the gasification reactivity of char (e.g. the degree of reaction taking place in a reactive atmosphere), and the relative reactivity of char as a result of its preparation conditions. The reactions of chars in a reactive atmosphere are discussed in 2.4.4.2 while the effect of char preparation conditions on its reactivity is discussed in 2.4.4.3.

2.4.4.2 Mechanism of the Gas Solid Reaction and Kinetics

2.4.4.2.1 Introduction

A general kinetic expression for the overall reaction rate can be written as:

$$\frac{dX}{dT} = r_s(p_i, T_p) f(X) \quad \text{Equation 1}$$

$r_s(p_i, T_p)$: is the intrinsic surface reaction rate depending on the partial pressure of the component i (p_i) and the particle temperature (T_p), $f(X)$ is a structure factor which describes the development of the total number of reactive sites per unit volume of char as a function of carbon conversion (X). To describe the change in surface area and pore structure a number of models are available. A good overview of the different models is given by Kristiansen [5]. The different approaches to model these reactions are summarised in three categories: (1) Grain model, in which particles are made up by agglomerated grains and the pores consists of the gaps between the grains. (2) Capillary model, which describes the particle as cylindrical pores with random intersections. (3) Percolation models, which employ a statistical approach to describe pore distribution.

2.4.4.2.2 Gasification with Oxygen

Carbon can react with oxygen either to CO_2 , complete combustion, or to CO , partial combustion. Because of the conditions in the gasifier (high temperature) all reactions with free oxygen can be considered to be complete (all available oxygen reacts) and do not need to be considered in determining the final syngas composition [7]. The exothermic combustion reactions with oxygen produce the heat needed for gasification. The amount of oxygen in the gasification agent therefore influences the temperature in the gasifier. Because reactions with oxygen are very fast, the carbon conversion in a gasifier increases with increasing partial oxygen pressure. However, this is outbalanced by the increasing concentration of CO_2 , which reduces the energy conversion and the heating value of the produced gas. Therefore the operating

conditions of a gasification process have to be very carefully adjusted and modified for each feedstock [5].

The primary ratio of CO and CO₂ during char oxidation is of interest for modelling of the gasification processes. Normally the factor Φ in Reaction 8 is treated as an adjustable parameter to express the ratio. It increases exponentially with temperature (and wherefore CO increases), decreases with increasing partial pressure of oxygen and is lower for coal containing high amounts of calcium. Despite these trends literature values were found to vary by several orders of magnitude as they seem to be specific for the particular char they have been developed. Values from 0.75 to 0.85 for Φ are recommended in literature [53-55].



2.4.4.2.3 Gasification with Carbon Dioxide

The gasification with carbon dioxide is usually the main gasification reaction. The reaction is endothermic, very slow below temperatures of 1000 K and inhibited by the product CO. Under the same conditions the reaction with CO₂ is several orders of magnitudes slower than the reaction with free O₂ [56]. Several reaction mechanisms for the gas solid reaction have been proposed. The mechanisms are based on the following surface reactions:



C(): active carbon site

C(O)/C(CO): oxygen/CO surface complex

The formation of an oxygen-surface complex due to the dissociation of a carbon dioxide molecule at an active carbon site and the release of a CO molecule is the first step (Reaction 9) in all proposed models [5]. Ergun [57] proposed an oxygen exchange mechanism which can be described by Reaction 9 and Reaction 10. An

oxygen atom is exchanged from the CO₂ molecule to a active side on the solid surface, forming an oxygen-surface complex (C(O)) and CO. This step is assumed to be reversible and inhibited by its product (CO). In a second, irreversible step a CO molecule and a new active side are formed. The C/CO₂ reaction rate is dependent on the partial pressures of CO and CO₂. The mechanisms can be described by a Langmuir-Hinshelwood type of rate equation [58]:

$$R_a = \frac{k_1 p(\text{CO}_2)}{1 + K_a p(\text{CO}) + K_b p(\text{CO}_2)} \quad \text{Equation 2}$$

$$K_a = k_{-1}/k_2$$

$$K_b = k_1/k_2$$

R_a: rate of consumption of carbon

A different reaction mechanism was proposed by Gadsby et al. [59] involving all three steps (Reaction 9, Reaction 10 and Reaction 11). Step 1 of the reaction is assumed to be irreversible and the inhibition is caused by the building of a C(CO) surface complex. Hampartsoumian et al. [60] obtained kinetic data from different UK coals for the char-CO₂ reaction to find out which of the two mechanisms controls the reaction. Reactivity data were obtained for atmospheric pressure and the temperature range of 973-1300 K. The data support an oxygen exchange mechanism (Reaction 9 and Reaction 10) as proposed by Ergun [57].

2.4.4.2.4 Gasification with Steam

The gasification with steam is in general considered to be faster at lower temperatures than the gasification with CO₂. As for the carbon-CO₂ reaction, different models have been proposed to describe the carbon-steam reaction mechanism. The following four reactions describe the different steps involved in the four proposed mechanisms [5]:



C(): active carbon site

C(O)/C(H): oxygen/H surface complex

All proposed models incorporate the first two steps (Reaction 12 and Reaction 13): The dissociation of a water molecule at a carbon active site, releasing hydrogen and forming an oxidised surface complex is the first step. Step 2, is the actual gasification of carbon. A carbon-oxygen complex subsequently produces a molecule of CO and a new active site [61]. The models are different in the way they account for the hydrogen inhibition. The following four different models are proposed, however the ‘first hydrogen/carbon monoxide inhibition model’ is the most popular one [5]:

- (1) *Oxygen Exchange Model:* The reaction in step 1 is assumed to be reversible, and the product of the reaction, hydrogen, therefore inhibits the reaction, by affecting the equilibrium of the reaction.
- (2) *First Hydrogen/Carbon Monoxide Inhibition Model:* The reaction in step 1 is assumed to be irreversible. Hydrogen inhibits the overall reaction by reaction with carbon active sites producing a $C(H)_2$ -complex.
- (3) *Second Hydrogen Inhibition Model:* The reaction in step 1 is assumed to be irreversible. The overall reaction is inhibited by chemisorption of hydrogen on carbon active sites.
- (4) *Combined Oxygen Exchange/Hydrogen Inhibition Model:* The reaction in step 1 is assumed to be reversible, and thereby inhibited by hydrogen. In addition hydrogen inhibits the overall reaction by reaction with carbon active sites producing a complex.

2.4.4.3 Influence of Char Production Conditions on Char Reactivity

2.4.4.3.1 Introduction

The effect of four char production operating conditions (temperature, pressure, heating rate and holding time) and of the particle size and coal rank on the char reactivity are reviewed in this section. The vast majority of the findings presented here are the results of a large number of projects at Imperial College London. To be able to concentrate on the key findings for each condition, the most important experimental set ups and their specific characteristics are briefly explained first.

- (1) High pressure wire mesh reactor [62]. A batch fuel sample of 5 mg is heated electrically between two layers of mesh. Heating rate (up to 10,000 K/s), temperature and holding time can be controlled accurately. Particles are separated from each other to rule out effects arising from particle-particle interaction. Volatile material released from the particles is immediately carried away by a sweep gas and condensed in the tar trap. Experiments at up to 2000°C, 100 bar with He, H₂, steam and CO₂ can be carried out.
- (2) High pressure fluidised bed reactor [36]. Batch samples of coal (50 – 200 mg) were injected via a water cooled probe into a bubbling fluidised bed. Volatile matter was carried out of the reactor and tar was condensed and could be collected. The reactor could operate at up to 1000°C and 40 bar with different gas compositions as gasification agent. Compared to the wire mesh reactor, tar had to pass through the bed and the free board before being condensed. This resulted in a higher degree of tar cracking but the total volatile yields were comparable.
- (3) Study by Cousins et al. [63-65]. A fluidised bed reactor with similar configuration to the one used in this work was used to investigate the effect of operating conditions (temperature, pressure, gas composition, holding time and particle size) on the char combustion reactivity. In this reactor configuration, gas and fuel were injected through a spout at the bottom of the bed. Batch coal samples were injected into a preheated fluidised sand bed before being discharged and quenched after a precise holding time. The char

was separated from the bed and its combustion reactivity measured with a TGA.

2.4.4.3.2 Temperature

Increasing temperature decreases the combustion reactivity of the produced chars. This can be explained by changes in char properties: Loss of active sites, decrease in hydrogen content and annealing of the char surface [66]. Messenbock [67] prepared char under CO₂ atmosphere in a wire-mesh reactor at temperatures of 850°C and 1000°C (heating rate 1000°C/s, holding time 10 s). For all six investigated coal samples the reactivity decreased with increasing temperature. These results were the same for 1 bar_g and 30 bar_g pressure. Cousins [63] prepared char under CO₂ atmosphere in a fluidised bed reactor at temperatures between 850°C and 950°C. The results also showed a decrease in char reactivity with increasing preparation temperature.

2.4.4.3.3 Pressure

Increasing the external pressure suppresses the release of volatiles. The suppression of volatile release reduces the diffusivity. Cracking of the volatiles on the hot char surface leads to the build-up of relatively unreactive secondary char on the surface of the primary char, reducing the reactivity. The most significant loss of reactivity occurs in the range of 1 to 10 bar_g. Above 10 bar_g the surface of the char is saturated and only minor changes take place [65, 68]. Chatzakis [69] used a fixed bed reactor to prepare char under CO₂ gasification conditions (850°C and 1000°C, heating rate 10°C/s, hold time 10 s). In his experiments char combustion reactivity decreased almost linearly as pressure increased from 1 to 30 bar_g. Despite the decrease in char combustion reactivity the extent of char gasification was found to increase with pressure as a result of increasing partial pressure of the gasification agent [70].

2.4.4.3.4 Heating Rate

The increase of particle heating rate has two major effects: (1) Completion of tar release is shifted to higher temperatures as the rate of temperature increase is overtaking the sequence of pyrolysis. For example, at heating rates around 1000°C/s

tar release reaches completion at 600 - 700°C while for slower heating rates (around 1°C/s) completion of tar release is reached between 550°C and 600°C [70]. (2) Faster heating of particles increases the amount of volatiles released. Rapid pressure build up inside the particles leads to fast ejection of volatiles and reduces the change of tar condensing in the particle pores [71, 72]. Less secondary char and a larger amount of volatile release at higher heating rates results in char particles with a high char combustion reactivity. In a fluidised bed reactor the heating rate is assumed to be between 500°C and 1000°C/s.

2.4.4.3.5 Holding Time at Temperature

The reactivity of char is strongly dependent on the time it is exposed to high temperatures (holding time). The majority of reactivity loss occurs in the first 10 sec. After 60 s the remaining char is reduced to a relatively un-reactive residue. External changes in morphology, such as change in pore size, are thought to be responsible for the early decrease in reactivity. The formation of graphite structures were identified as reason for continuing loss of reactivity after the first minute. The reactivity data obtained from the bench scale reactors were used to explain the very low reactivity of char recovered from the ABGC. It was found that by simulating the conditions in the ABGC gasifier more closely in the bench scale reactors, i.e. larger particles (> 600 µm) and long residence times (> 1 h), the bench scale measurements were approaching the values from the pilot scale and the very low char reactivity could be simulated [65, 70, 73, 74].

2.4.4.3.6 Particle Size

Reactivity of char particles decreases with particle size. On the one hand volatiles are more likely to crack inside the pores if the particles are larger and depositing a layer of un-reactive secondary char on the surface. Zhuo et al. [74] found that larger particles (600 – 850 µm) release 6% less volatiles than smaller particles (105 – 150 µm) as a result of volatiles condensing inside the pores in a wire mesh reactor. Cousins et al. [65] investigated the influence of particle size on char reactivity in a bench scale fluidised bed reactor. Daw Mill Coal samples with particle size ranges of 106-150, 250-425, and 600-850 µm were injected into the preheated sand bed of the reactor at 950°C and 13 bar_g in N₂. It was found that for all residence times, the char reactivity decreases with increasing particle size. These results are consistent with the

results obtained by Megaritis et al. [36] using a previous configuration of the fluidised bed reactor. Another issue related to particle size is the fact that larger particles simply require more time to be consumed by gasification reactions than smaller particles. Therefore char of larger particles ages and its reactivity decreases. As discussed before, after 60 s exposure to high temperatures, char reactivity is very low.

2.4.4.3.7 Coal Rank

The rank of coal has apparently the biggest influence on the char reactivity [75]. Relevant fuel properties are: crystallite structure of the carbon, pore structure, catalytic effect of minerals and grain size [6]. Coal with a high volatile matter (low rank) produces char with a big surface area during pyrolysis due to the higher number of channels caused by escaping volatiles. Bigger surface area means more active sites are available for the gas-solid gasification reaction. Therefore the char reactivity in general increases with decreasing coal rank [48, 76-78]. An example of the effect of coal rank on gasification reactivity is given in Figure 5. It shows the gasification reactivity for the steam-char reaction for different fuels. It can be seen that the reactivity increases from hard coal to brown coal to biomass.

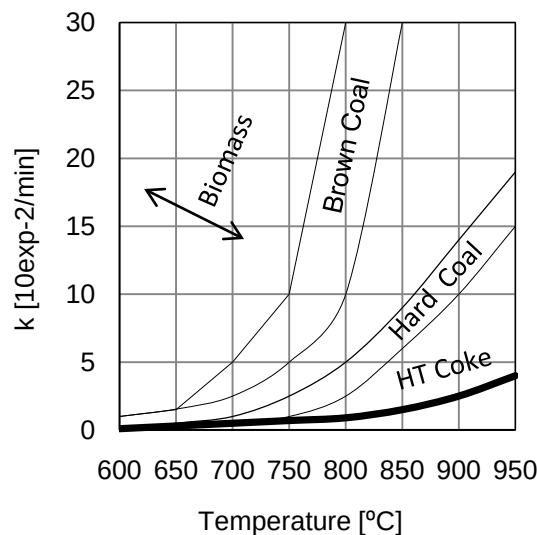


Figure 5: Reactivity of different solid fuels for the water-gas reaction at 4 MPa [6].

2.4.5 Catalytic Gasification of Solid Fuels

A large number of metals and metals oxides are identified as catalysts for the carbon- CO_2 and carbon-steam gasification reactions [79-82]. The metal content can either come from the inorganic material of the fuel itself or can be added to the fuel. It is generally accepted that carbon gasification proceeds via $\text{C}(\text{O})$ surface complexes formed by oxygen exchange mechanism and the formation of these complexes is catalysed by the metal atoms or metal oxides. The following catalytic reaction mechanism for the metal-catalysed CO_2 gasification of coal char was proposed by Sears et al. [83] and Moulijn et al. [84]:



$\text{C}()$: active carbon site

M: metal atom

$\text{MO}(\text{O})/\text{C}(\text{O})$: surface complex

‘White spots’ on the char surface seen with SEM analysis were identified as activation centres formed by catalytic material [85]. These activation centres are the exchange points for the formation of oxygen surface complexes [86] and believed to be the reason for the catalytic activity.

The most important catalytic effect for this study is the effect of calcium on the char- CO_2 reaction as CO_2 is used as main gasification agent and CaCO_3 is added for a number of experiments. The active form of Ca is thought to be highly dispersed CaO [87]. The isothermal CO_2 reactivity of pure polymer carbons for different Ca loading was studied by Delecea et al. [88] and Linaressolano et al. [89]. The reactivity of the char was found to increase almost linearly with Ca content up to about 4%. After that no effect of Ca loading was detected.

2.4.6 Co - Processing of Coal and Biomass

Increasing costs for landfill depositing and increasing public, political and economical pressure to reduce greenhouse gas emission have increased the interest in co-processing of biomass and waste with coal. Gasification of biomass can be seen as CO₂ neutral and reduces the dependence on fossil fuels [70]. It could be expected that co-processing two different types of fuel would combine the characteristics of both and the resulting synergistic effects could be used for process optimisation. For example the large amount of tar produced during biomass gasification could be reduced by co-gasification with coal. On the other hand, the relatively low reactivity of coal could be increased by co-processing with highly reactive biomass leading to an increase in overall carbon conversion. Conflicting reports have been published either proving the existence of synergetic effects or concluding that there are no such benefits. For example, Sjöström et al. [90] reported higher carbon conversion due to co-gasification of a Polish coal with silver birch wood in a pressurised fluidised bed reactor (4 bar_g, 700 - 900°C). In this experiment, a sample was continuously fed into a sand bed at a rate of 27 - 87 g/min. The authors found lower char yields and higher oxygen consumption than expected for a comparable gasification of the single fuels. It was concluded that the higher reactivity of wood increases the overall fuel reactivity. By contrast, work carried out in Imperial College Energy Engineering group by Collot et al. [91] found that neither intimate contact between fuel particles (fixed bed reactor) nor relative segregation of fuel particles during pyrolysis and CO₂ gasification affected total volatile release from mixed fuels. For these experiments 50:50 (w/w) of Daw Mill coal and silver birch wood were processed using a bench scale hot rod reactor (fixed bed) and a bench scale fluidised bed reactor (similar to the one used in the present work). Experiments were carried out at 850°C and 1000°C at elevated pressure (5 bar_g, 10 bar_g, 20 bar_g).

However, even in the absence of synergetic effects, co-gasification can be a very useful way of waste processing. For example, André et al. [92] reported successful co-gasification of coal with olive bagasse, a waste material from the olive oil industry. In that study, an atmospheric pressure fluidised bed reactor with 70 mm internal diameter was used. A low quality, high ash lignite from the Puertollano mines in Spain was used. The bed was fluidised on a mixture of air and steam in various

concentrations. The results suggested that up to 40% biomass by weight can be gasified together with coal. For values higher than that, the increasing tar evolution becomes an operational problem and decreases the efficiency. Raising the temperature to 890°C reduced the release of undesired hydrocarbons by 55% and increased hydrogen concentration. Higher temperatures could be achieved by raising the air flow rate although leading to N₂ dilution of the fuel gas and a decrease in the heating value of the produced gas.

2.4.7 Emissions of the Gasification Process

2.4.7.1 Tar

Production of a tar-free gas from a gasifier is clearly desirable. Producing tar decreases coal to gas conversion and causes problems with fouling. In entrained flow reactors a tar free gas is produced due to the very high temperatures of the process. Tar yield from gasification in a fluidised bed reactor is expected to be low due to tar cracking in the freeboard and fluidised bed itself. Megaritis et al. [36] compared the tar yield from a batch fed fluidised bed reactor and a wire mesh reactor. They found an approximately 20% lower tar yield in the fluidised bed reactor over the pressure range from 1 - 30 bar_g. In the wire mesh reactor, tar is rapidly pushed out from the hot zone into the tar trap while in the fluidised bed reactor the tar is carried by the gas stream through the freeboard, which has a similar temperature to the bed. Tar yield was also found to decrease with increasing pressure. A reason could be that high pressure suppresses the release of lighter fragments from the particle pores and a higher rate of cracking occurs already in the channels prior to the release of any gaseous products [65, 68].

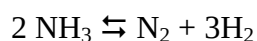
2.4.7.2 Nitrogen – Compounds

Nitrogen in coal: Coals contains typically 1 - 2.5 wt% of nitrogen, mainly in organic form. It is found as pyridinic (20 - 40%), pyrrolic (50 - 80%) and quaternary functional groups in polycyclic aromatic compounds (20%). The nitrogen content tends to increase with rank, reaching a maximum at about 80 to 85 wt% carbon and decreasing towards the anthracites [93].

Fate of nitrogen during gasification: Upon injection of coal into the gasifier pyrolysis products are released from the fuel particles. Between 40% and 60% of original fuel nitrogen [70] is released as pyrrolic and pyridinic nitrogen [94] during this process. Under the conditions in the fluidised bed gasifier, fuel rich and elevated temperature, the fuel-nitrogen derived compounds break down to release mainly HCN together with small quantities of NH₃ [95, 96]. During the gasification of the remaining char, fuel-nitrogen is either released as N₂ or NH₃.

The nitrogen compounds are released in the oxygen rich region of the gasifier around the inlet zone. For a spouted bed gasifier this would be in the immediate spout region. Therefore any species formed there would have to pass through the reducing atmosphere in the rest of the bed and in the freeboard before being released into the fuel gas stream. In comparison to combustion processes this leads to decreases in NO_x emissions as the formation of reduced species, NH₃ and HCN, is more likely [97].

Pressure: Increasing pressure has two separate effects on the concentration of nitrogen compounds: Firstly, pressure diminishes the release of volatiles from the fuel particles. Therefore the residence time of gaseous material in the porous structure is increased and more HCN is converted to NH₃ by the reaction with hydrogen [70]. Secondly, following the Le Chatelier's Principle, the equilibrium of Reaction 19 is shifted to the left. [98]. Both effects lead to a higher NH₃ concentration in the fuel gas at elevated pressure.



Reaction 19

Temperature: In the temperature range of 600 - 1000°C the NH₃ concentration seems to go through a maximum [98-100]. It was concluded that higher temperatures lead to higher rate of reaction and the actual concentrations are closer to the equilibrium concentration.

Steam: The presence of steam increases the NH₃ concentration in the fuel gas [25, 101]. Steam is thought to hydrogenate the nitrogen in coal [99].

Nitrogen emissions: It is desirable to remove any nitrogen-species in the fuel gas before it is used in a gas turbine or chemical synthesis. While only little or no NO_x is produced during gasification, HCN and NH_3 are oxidised upon combustion and therefore considered as NO_x precursors. Any subsequent catalytic process nitrogen species can act as a poison, for example HCN for a Fischer-Tropsch catalyst. Due to their high solubility, NH_3 and HCN can be easily removed with a water wash stage. However it has to be considered that the regeneration of the water is equally difficult.

2.4.7.3 Sulphur – Compounds

Introduction: In this section the fate of fuel sulphur during gasification is discussed. First the origin of sulphur in coal is reviewed, and then the current emission targets are discussed followed by the chemistry of sulphur in reducing atmospheres. Strategies of gas cleaning and in bed sulphur capture are reviewed together with trends in sulphur release with changing gasification conditions.

Sulphur in coal: Different types of coals can be classified by their sulphur content into three categories [102]: Low sulphur content (< 1%), medium sulphur content (1 - 2%) and high sulphur content (> 3%). The sulphur in coal exists in inorganic, organic form and in some cases as elementary sulphur. Inorganic sulphur is mainly composed of minerals like pyrite or marcasite, sulphates like BaSO_4 and CaSO_4 and sulphide of zinc and lead. Organic sulphur in coal exists in the form of aliphatic, aromatic and thiophenic sulphur while the majority of sulphur is in the form of pyrite. Low sulphur coals have their sulphur content mainly from the sulphur components in the coal-forming plants. High sulphur coals obtained their sulphur mainly from the reduction of sulphate ions in sea water by microbial processes. The produced H_2S is either chemically incorporated into the peat or reacts with ferric ions in the water to form pyrite [103].

Sulphur emissions: Sulphur containing compounds in the flue gas of a gasifier have to be avoided for a number of different reasons. High sulphur content of the raw syngas can lead to corrosion issues as well as cause catalyst poisoning in downstream catalytic processes. In the case of an IGCC plant, damage of the gas turbine by sulphur compounds has to be avoided as well as emissions in the flue gas have to comply with current legislation. In order to achieve a SO_x value comparable to modern power plants with flue gas desulphurisation units, the raw gas from the gasifier in an IGCC plant has to be lowered to < 10 ppm (vol.) prior to combustion [104]. A number of well proven technologies are available to clean the raw gas. An example is the Rectisol® process using cooled methanol to absorb the sulphur [7, 105, 106]. In subsequent processes, the sulphur can be collected as elementary sulphur (Claus Process [107]). However gas cleaning is always associated with loss of plant efficiency and increased capital costs. Therefore it is desirable to minimise the

sulphur content in the raw gas by choosing optimum operating conditions and in case of fluidised bed gasifier retaining a maximum amount of sulphur in the bed.

Fate of sulphur during gasification: Sulphur released from the coal is converted under the reducing atmosphere in a gasifier mainly to H₂S and a smaller amount of COS. The equilibrium between this two species is controlled by the hydrogenation reaction (Reaction 20) and the hydrolysis reaction (Reaction 21) [7]:



H₂S is the major sulphur species in the gas phase under reducing conditions typical for gasification processes [7, 55, 100, 108, 109]. Besides H₂S, a certain amount of other sulphur species can be formed depending on the conditions. Higher partial pressure of CO₂ promotes the formation of COS while increasing partial pressure of steam promotes the H₂S formation [110]. For lower ranked coal with higher char reactivity the formation of CS₂ by the reaction of char with H₂S can become significant [109]. SO_x can be formed by direct combustion with free O₂ from the fluidising gas. Sciazko et al. [111] studied the release of S-compounds from partial gasification of coal in a circulating fluidised bed (scale: 300 kg/h of coal). At coal/air ratios from 0.9 to 1.1 they recorded 80% of the released sulphur as H₂S and 20% as SO₂ and SO₃. Even higher amounts of SO_x were found by Qi et al. [112]. They investigated the effect of temperature, residence time and atmosphere on the sulphur release during pyrolysis of two Chinese coals in a fluidised bed. Their experiments with Ar-O₂ mixtures showed that a maximum of 50% of the sulphur was released as SO₂.

The gaseous atmosphere does not only affect the sulphur distribution in the gas phase but also the extent to which the sulphur is released into the gas phase. Increased concentrations of H₂ and steam increase the extent to which sulphur is gasified, mainly because of the decomposition of thiopenic structures at lower temperatures [108, 113]. In terms of the influence of temperature¹ on the sulphur release four main

¹ Only range relevant of fluidized bed gasification is considered here

observations are reported [112, 114-116]: (1) at lower temperature the sulphur in the gas phase comes from the inorganic sulphur content (mainly pyrite) of the fuel, (2) at higher temperatures the organic sulphur decomposes and it is released into the gas phase (3) With increasing temperature the extent of reaction of sulphur in the gas phase (mainly H₂S) with the inorganic compounds of the coal increases. (4) The effect temperature has on the sulphur release varies with different fuels as it depends of the type of organic sulphur and the amount and type of ash in the fuel. In summary, it can be said that with increasing temperature these are two opposing effects, the increased release of organic sulphur and the increased sulphur capture by the ash. As a result for each fuel the sulphur release goes through a maximum at a certain temperature.

In bed sulphur retention: Fluidised bed gasifiers are the gasifier of choice to process coals high in sulphur. Between 70 - 80% of sulphur retention can be achieved by adding limestone or dolomite to the bed material [117]. Compared to Dolomite (CaCO₃ MgCO₃), Limestone (CaCO₃) has certain advantages. MgO is already formed at very low temperatures but its reaction with H₂S is too slow to be effective for sulphur capture. However the escaping CO₂ forms a porous material which increases the efficiency of the sulphur capture. [97]. According to Reaction 21 the hydrogen sulphide in the gas phase is reacting with calcium oxide to solid calcium sulphide. COS could also be captured by CaO (Reaction 22) [118].



The reactions above assume that the operation temperatures in the gasifier are high enough to calcine the CaCO₃ (Reaction 24). If that is not the case, the direct sulfation of CaCO₃ is also possible, but at a much lower rate (Reaction 25) [119].



Research has shown that maximum sulphur absorption occurs at the calcination equilibrium temperature [120]. The maximum can be explained by the difference in temperature dependency of the two sulphur absorbing reactions. The direct sulfation

(Reaction 25) is endothermic; the indirect sulfation (Reaction 22) is exothermic. It has also to be considered that sulphur capture increases the CO₂ emissions as one mole of sulphur captured implies one mole of CO₂ released. In addition, 3 - 4 times the amount of CaCO₃ has to be used for the absorption process to be effective [97].

2.4.7.4 Trace Elements

Coal contains major elements (C, H, O, N and S), minor elements (Al, Ca, Fe, K, Mg, Na and Si) and trace elements (all remaining elements with content below 1000 ppm). Table 3 gives ranges of concentrations of selected trace elements.

Table 3: Typical concentrations range (ppm) of six trace elements in coal [121]

Elements	Coal [ppm]
Arsenic	0.5 – 10
Cadmium	0.05 – 10
Lead	1 – 300
Mercury	0.02 – 3
Selenium	0.2 – 3
Zinc	1 – 100

Because of the large amounts of coal processed in pf power plants and gasifiers, the toxic elements present in coal in concentrations in the ppm range are emitted in considerable quantities. For example in 1999, 900 Mt of coal were consumed by US power plants and 75 t of mercury were released to the atmosphere [122]. In terms of regulations, the Environmental Protection Agency (EPA) in the United States issued mercury standard emissions limits. Under these regulations, IGCC power plants will have some of the strictest limits [123]. It is clear that trace element releases from coal gasification have to be addressed if future power generation will be based on such technologies.

2.5 Examples of Fluidised Bed Gasification Processes

2.5.1 Introduction

A number of fluidised bed gasification processes have been developed over time. However development stopped at pilot/demonstration scale as the interest in gasification declined in the 1980s. This section gives an overview of a number of different coal gasification processes developed. It has to be noted that it is not the intention to provide a complete list of all fluidised bed processes. The aim is to review processes relevant for this project and to give an indication about the scale, performance and configuration of a number of different fluidised bed gasifiers.

The first gasification process based on a fluidised bed concept was the atmospheric pressure Winkler gasifier. The patent was filed in 1922 and the first plant built in 1925. Around 70 plants have been built since then. However all of them are now shut down due to economic reasons. The gasifier was oxygen/steam blown and used to gasify a whole range of different coals. Especially with high ranked coals the carbon conversion was low (80%) and the ash had to be burned in an auxiliary burner. The subsequent developments of fluidised bed gasification were influenced by the success of the Winkler concept [7, 17, 124].

2.5.2 High-Temperature Winkler (HTW) Process

Rheinbraun Brennstoff GmbH developed a high pressure process based on the original Winkler process. The gasifier is fluidised with either air or oxygen/steam. The bed temperature is kept at about 800°C, below the ash fusion temperature [125]. The process was originally designed for processing highly reactive lignites, allowing relatively low gasification temperatures, and therefore reducing the cost of oxygen production. Injecting additional gasification agent at the height of the freeboard, raises the temperature in this section to 900 - 950°C, eliminating undesired by products and increasing carbon conversion [126]. The process operates at elevated pressure between 10 - 30 bar_g.

A 25 bar 160 t/d, pilot plant in Wesseling was built in 1989 to demonstrate various aspects related to IGCC applications, but is now shut down [7]. The plant had a

maximum thermal capacity of 36 MW and was operated with air blown and oxygen/steam conditions. A wide range of coals were successfully tested in the system proving the flexibility of fluidised bed gasification. Not only could lignite be successfully processed, but it was also possible to use hard coal with lower char reactivity. The high ash fusion point allowed the temperature to be raised to 1000°C ensuring sufficient carbon conversion.

Currently there are plans for a 400 MW IGCC plant to replace 26 Lurgi-moving beds at Vresova in the Czech Republic. The plant would operate under 30 bar pressure with Czech lignite as feedstock [127]. Among several other new developments, an ammonia recycle loop will be included. Ammonia separated from the flue gas will be recycled back into the gasifier and converted into nitrogen and hydrogen [1].

Bhattacharya [101] discussed the gasification performance of Australian lignite in a high temperature Winkler (HTW) gasification process development unit. The coal was pre-dried to less than 20% moisture and tests were carried out at 8 bar_g and an average bed temperature of 750 - 920°C. The bed was either fluidised on air/steam or oxygen-enriched air/steam. A carbon conversion of 70 - 85% was achieved depending on the feedstock and operational parameters. Two main factors were identified as causing low carbon conversion: (1) a high percentage of fines in the bed leads to an increase in carbon losses due to fine particles with a high carbon content being carried out of the reactor by the gas stream. Removing these fines beforehand increased the carbon conversion. (2) When operating the gasifier with coals high in ash, a more frequent draining of the bed is required. In a well mixed bed this leads to carbon losses.

Regarding gas compositions, concentrations of CO, CO₂ and H₂ increased with increasing temperature and increasing percentage of O₂ in the feed gas. The concentration of CH₄ was invariant as it is mainly a result of pyrolysis. The methanation reaction ($C + 2 H_2 \rightarrow CH_4$) is a function of pressure and only becomes important above 15 bar_g. Increasing the freeboard temperature above the bed temperature with additional injection of air/O₂ and steam increased the total amount of combustibles in the flue gas. It was suggested that this was because of additional

steam gasification of entrained fines and, to a lesser extent, because of additional water-gas shift reaction.

Greaebner et al. [128] presented a numerical simulation of coal gasification at circulating fluidised bed conditions. The calculations are based on a 1000 MW power plant with an O₂/steam blown gasifier with a throughput of 4800 t/d of lignite operating at 33 bar. The model is based on a newly developed gasification concept called the PHTW process (Power High Temperature Winkler). It is a combination of a slagging fixed bed gasifier at the lower section and a fluidised bed at the top section. Pyrolysis and the majority of the char gasification are expected to take place in the fluidised bed while the high temperatures in the slag bath ensure conversion of any residual carbon. The simulation predicts a well mixed bed with an average temperature of 960°C and a maximum temperature of 2600°C near the O₂ injection nozzles. According to the authors the developed model can be used for the assessment of new gasifier concepts.

2.5.3 Spouted Bed Configuration

2.5.3.1 Introduction

Spouted bed coal gasification at the pilot scale was successfully investigated in the UK [129-131], Canada [132-140] and Japan [141]. At the demonstration scale, spouted bed technology was used in the Kellogg Rust Westinghouse (KRW) process for the 100 MW Pinon Pine IGCC power plant, built by South Pacific Power Company in 1998.

2.5.3.2 The Pilot Plant of the University of Columbia, Canada

Watkinson et al. [138] were investigating the flue gas composition of an atmospheric pressure spouted bed reactor (0.3 m i.d.). The gasifier is fed with 50 kg/h of bituminous or sub-bituminous coal and air, oxygen and steam were used as gasification agent. The initial bed material was either inert material like sand or char from previous experiments. Carbon conversion was calculated based on CO, CH₄ and CO₂ content of the gas. A constant carbon conversion of 64.6% was archived. Typical

values for the flue gas composition of an oxygen-steam blown run on dry base are: 36.5% H₂, 32% CO and 27.8% CO₂. The gas has a heating value (LHV) of 9.25 MJ/m³. A slightly higher carbon conversion was achieved with a bed of inert material. It was concluded that the inert material is changing hydrodynamic conditions in the bed towards a better gas solid contact.

2.5.3.3 Air Blown Gasification Cycle (ABGC)

The ABGC process was developed between 1990 and 1997 by British Coal in the UK. A pilot scale gasifier (0.5 t/h) was constructed in Stoke Orchard, Gloucestershire. The rights are now owned by Doosan Babcock Energy Ltd (DBEL). The pilot gasifier was a pressurised spouted bed reactor that used air as fluidising agent. It was operated at pressures up to 25 bar_g in the temperature range of 900 - 1000°C. The design is based on 80% carbon conversion in the gasifier with the remaining carbon burnt in a circulating fluidised bed combustor. The hybrid cycle of gasification and combustion was forecast to have an efficiency of about 46 - 48%. The ABGC technology was later used by DBEL in collaboration with GEC ALSTHOM (ALSTHOM Power) and Scottish Power plc to develop an advanced design of a demonstration plant. In the moment there is no plan for future commercial-scale development [1].

2.5.3.4 Kellogg Rust Westinghouse (KRW) Process

The Kellogg Rust Westinghouse process was used in the 100 MW Pinon Pine IGCC power plant build by South Pacific Power Company in 1998. The demonstration plant was estimated to have an efficiency of 40.7% (HHV basis). However, problems such as fines bridging in vessels, have prevented coal feeding for more than 6 - 8 hours continuously. The project was considered to be unsuccessful, although the gasifier worked without major problems [142].

It employed a pressurised fluidised bed gasifier where coal and limestone (both grinded < 0.8 mm) enter the reactor through a central spout. The reactor operated at up to 20 bar_g pressure and was fluidised with air and steam. The bed is fluidised on air and steam in a way that the temperature around the gas nozzle is raised above the ash fusion temperature (ash agglomeration conditions). Large agglomerated ash particles

are formed and because the gas velocity in the bottom part of the reactor is between the minimum fluidising velocity of the char and the agglomerates, the latter sink to the bottom and can be removed from the reactor. Allowing the temperature to rise above ash fusion temperature (maximum temperature in the bed 1150 - 1260°C) led to a high carbon conversion (90 - 96%) during test with bituminous coal in the Pinon Pine plant [1]. The ash, residual carbon and the sulphided limestone were burned in a fluidised bed combustor.

2.5.3.5 Modelling of Spouted Bed Gasifiers (Selected Examples)

Two examples for the modelling of spouted bed gasifier were selected from the literature. These examples were chosen as experimental data were used to verify the calculations and the results provide an insight into different aspects of spouted bed gasifier, which are not accessible by experimental measurements.

The work by Luo et al. [143] presents the results for modelling a jetting fluidized bed gasifier. The shape of the fluidised bed reactor is similar to the one used in this project. The base of the bed is an inverse cone with a steep angle of 60°. For the calculations, the reactor is divided into three parts: grid zone with the conical shape and the spout, bubbling fluidised bed and free board. The experimental work is carried out in an electrically heated stainless steel reactor with a bed height of approximately 16 cm operating at 1123 K. Coal is fed from the top. The bed is fluidised on a mixture of steam and air. The reactor is fitted with a number of gas sampling probes allowing measuring the gas composition at different bed heights and different axial positions. With the model it is possible to estimate the amount of carbon converted in the different reactor sections. It was found that the majority of the carbon conversion takes place in the spout and to a smaller extent in the bubbling bed. The simulation also includes change of particle temperature with bed height. The results show that in the zone where O₂ is entering the reactor, the particle temperature is high due to the oxidation. With increasing bed height the particle temperature decreases as the endothermic gasification reactions is the main reaction taking place. A high concentration of CO₂ as a result of combustion was predicted by the calculations and confirmed by measurements. The results also show that the influence

of the primary ratio of CO/CO₂ from combustion has only a small influence on the final results.

The work by Lucas et al. [136] describes the development of a model of the spouted bed reactor used in the pilot plant at the University of Columbia (reactor discussed above). Coal is fed through the conical spout area and fuels are gasified either with O₂/steam or air/steam. The most interesting results are obtained by varying the height of the bed in the model. Low beds were found to have a reduced recirculation rate in the bed resulting in a decrease in gas solid contact and in an increase of the temperature at the spout. Therefore the bed height has to be balanced on the one hand to achieve necessary temperatures required for high carbon conversion and on the other hand to keep the maximum temperature below the ash softening point.

2.6 Summary

The need for highly efficient processes to convert coal into energy while keeping CO₂ emissions at minimum is the main driving force behind the development of novel gasification concepts. The integration of carbon capture and storage technology is changing the design framework for gasification plants. The main objective of these new developments is to reduce the energy penalty associated with CCS technology. Therefore the focus of new gasification concepts is on the integration of CCS. In the case of the proposed oxy-fuel fluidised bed gasification process this means to use the CO₂ to replace steam and/or nitrogen as gasification agent, temperature moderator and fluidising agent.

Air/steam and oxygen/steam blown fluidised bed gasification are proven technologies; however its large scale commercial use stopped with the decommissioning of the Winkler gasifiers. Since then a number of technologies were developed to pilot (e.g. ABGC gasifier) and demonstration scale (e.g. high pressure Winkler gasifier, KRW gasifier) but failed to penetrate the market. The improved integration of an oxy-fuel gasifier with CCS technology plus its advantages of processing low value coals, biomass and waste fuels has the potential to make fluidised bed gasifier an attractive option for future large scale power generation.

In this chapter the available information on gasification of solid fuels was summarised and discussed. This included pyrolysis, thermodynamics, mechanism of the gas solid reaction, char reactivity, catalytic aspects of gasification and pollutants from gasification processes. In addition recent developments of gasification processes with recycled CO₂ and a number of gasification modelling concepts were reviewed. From this information it becomes clear that due to the complexity of any gasification process, the development of a new concept requires extensive research and development at every scale. For the proposed oxy-fuel fluidised bed gasification process it is necessary to investigate the fundamentals of such processes as the high partial pressure of CO₂ changes the chemical and physical properties compared to air/steam and oxygen/steam blown gasification.

3 Experimental

3.1 Experimental Set Up

3.1.1 Introduction

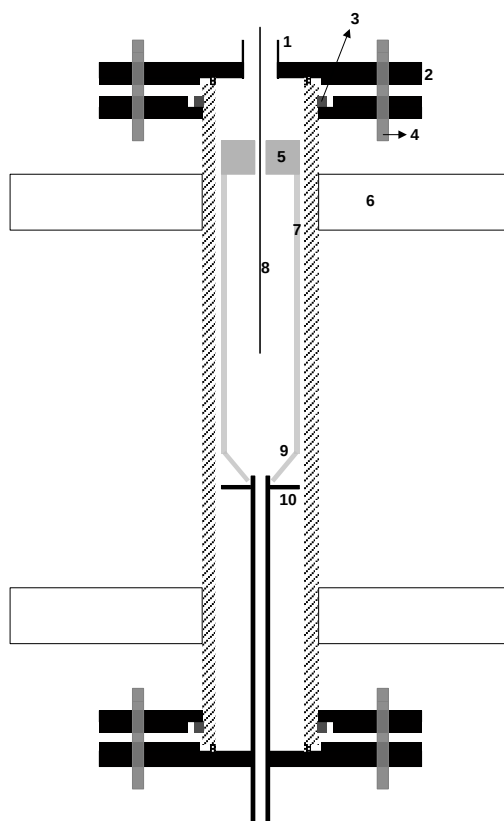
This section describes the experimental set up used in this project. A complete flow sheet with all parts listed and all valves is shown in Figure 9 at the end of this section. The modification and development of the reactor, fuel feeding system, upstream and downstream equipment, data acquisition and resistance heater are discussed in detail in this chapter together with the implication of oxy-fuel gasification conditions on the construction. An existing laboratory scale fluidised bed reactor was modified to work in continuous mode under oxy fuel conditions. Initially the reactor was developed for batch experiments [36, 73]. Further modifications included a system for continuous feed, the use of a spouted bed instead of a fluidised bed and online gas analysis [25, 98, 144]. The principal set up proved to be of great flexibility as it is relatively easy to adapt it to the specific requirements of each project [145, 146]. A more detailed report about previous work based on the same hardware platform was published by Cousins et al. [147]. The starting point for this project was the reactor configuration used to investigate the char reactivity in air blown gasification systems [64, 65].

3.1.2 High-Pressure Fluidised Bed Reactor

The reactor consists of a 34 mm (i.d.), 504 mm (tall) Incoloy 800 HT column, which acts as both pressure shell and resistance heater. A schematic diagram of the reactor is shown in Figure 6. The system is capable of operation at temperatures up to 1000°C (wall temperature) and 30 bar (see Appendix B, page 244, for high pressure safety calculations). To decrease the time necessary for heating, the reactor body is insulated with several layers of insulating material (Superwool 607™ MAX Blanket). A 28 mm (i.d.) quartz glass liner within the pressure tube contains the actual bed. At the bottom end the glass liner has been modified to give an inverted conical section with a hole at the apex. The spout jet, which feeds the coal and spout gas into the bed, fits into the hole at the base of the cone. To ensure a tight fit of the glass liner onto the spout, several layers of quartz paper were used as a seal. In addition, a counter weight placed on top of the glass liner was used to press it down (Figure 6). The counterweight is a

20 mm stainless steel disk (32 mm diameter) with a 12.5 mm hole. At the beginning of this project, a spring loaded system was used instead of the counter weight. It consisted of two rings (32 mm o.d., 29 mm i.d., 2 mm height) connected with four 40 mm steel springs. This assembly was placed on the top of the glass liner and was compressed when the top flange was closed. However, as it was found that a significant amount of tar evolved during the experiment condensed on the springs, it was replaced by the counterweight.

The flange at the top connects with the gas exit line, the bottom flange holds the fuel and gas spout line in place. Flanges and reactor are sealed using copper gaskets (40.5 mm i.d., 48.5 mm o.d., 1.5 mm thickness). It was found that the copper rings hardened very quickly by the compression pressure and had to be replaced after each run. The flanges are held in place by two half moon rings fitting into grooves machined in the reactor shell (Figure 6). Bolts are used to hold the flanges together (8 bolts each, M10, 50 mm, A4 stainless steel).



(1) Gas outlet line, (2) Flange, (3) Half moon ring, (4) Bolt, (5) Counter weight, (6) Electrode, (7) Quartz glass liner, (8) Thermocouple, (9) Conical shaped base, (10) Spout line

Figure 6: Schematic diagram of the high pressure fluidised bed reactor

3.1.3 Fuel Feeding System

For the current study the maximum feeding rate of the custom-made rotary valve was increased from 3 g/min to 6.5 g/min by increasing the internal volume of the valve and increasing the rotation speed. The improved performance increased the mechanical wear. Therefore a new version was developed, based on a simpler design, making it possible to replace the valve on a frequent basis (modified $\frac{1}{4}$ in plug valve, SS-4P4T, Swagelok). A schematic drawing of the current and the previous version is shown in Figure 7. A variable speed DC motor is used to drive the valve. The feeding rate is controlled by varying the rotation speed of the valve. The previous system [25] of two feed hoppers and a surge hopper was removed and replaced by a single hopper directly above the rotary valve. This eliminated problems with blockages in the feeding system. The fuel size range of 200 - 300 μm used in previous studies was found to be the most suitable for the feeding system. The presence of larger particles led to the blocking of the feed pipe, whilst smaller particles led to fines bridging in the feed hopper. To equilibrate the pressure between storage hopper, rotary valve and spout line, the top of the hopper is connected to the gas supply line of the reactor.

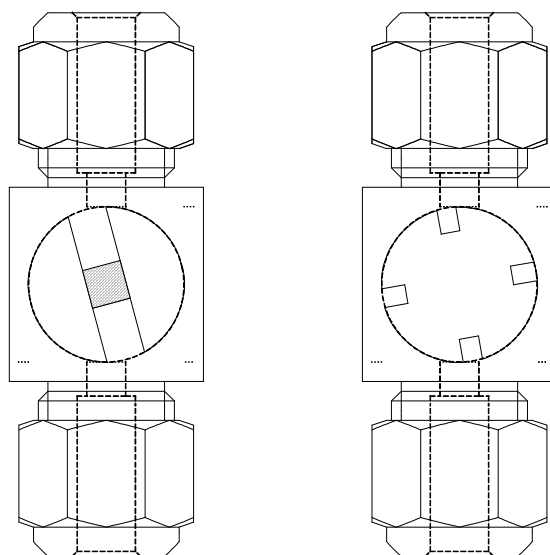


Figure 7: Left – Current version of the rotary valve. Right – previous version of the rotary valve.

3.1.4 Gas Cleaning, Tar Trap and Fuel Gas Incinerator

The hot gas stream from the reactor has to be cooled and tar, fines and moisture have to be removed before it enters the online gas analysers. To cool the gas and condense the tar and moisture, a new tar trap was designed. In a previous project, liquid nitrogen was used as the cooling agent. Initial tests have shown that this would cool

the temperature of the gas too close to the freezing point of CO₂. To prevent the possible condensation of CO₂, an ice/saline bath was used in the new tar trap. This however required a larger cooling area to achieve efficient cooling. The new tar trap was constructed from a ½ inch stainless steel tube, surrounded by a custom made stainless steel container. The container can be filled from the top with water, ice and salt, while the valve at the bottom enables draining of warm water during experiments. By doing so, the temperature of the cooling agent could be kept between +5 (top) and -10°C (bottom). This has been proven to be sufficient to cool the gas to ambient temperature. The gas exit temperature is constantly monitored during each experiment. The inside of the tube is packed with two large rolls of wire mesh to increase the heat transfer from the cold wall to the hot gas and provide a surface for condensation of the tar. During initial tests, it was found that condensed tar was carried out of the tar trap by the high velocity of the gas stream. Several layers of glass wool were therefore placed at the end of the trap. After this modification, no tar or particles were found in downstream equipment after the tar trap.

After the tar trap the gas passes through two high pressure bubblers, similar to glass Dreschel bottles. The first bubbler is filled with 100 ml deionised water to absorb remaining NH₃ in the gas, while the second one is empty and cooled with ice/water/salt to condense and collect remaining moisture in the gas. A high pressure stainless steel filter filled with glass wool and an additional low pressure filter cartridge were installed downstream as an additional safety measure. The gas sample stream to the online gas analyser passes through a tube filled with silica gel to further dry the gas. Before the gas is passed into the ventilation system it is burned using an auxiliary propane burner. Figure 8 shows the fuel gas from the gasifier being combusted into the ventilation hood using the propane burner. The large flame in the middle is the burning high velocity fuel gas stream.

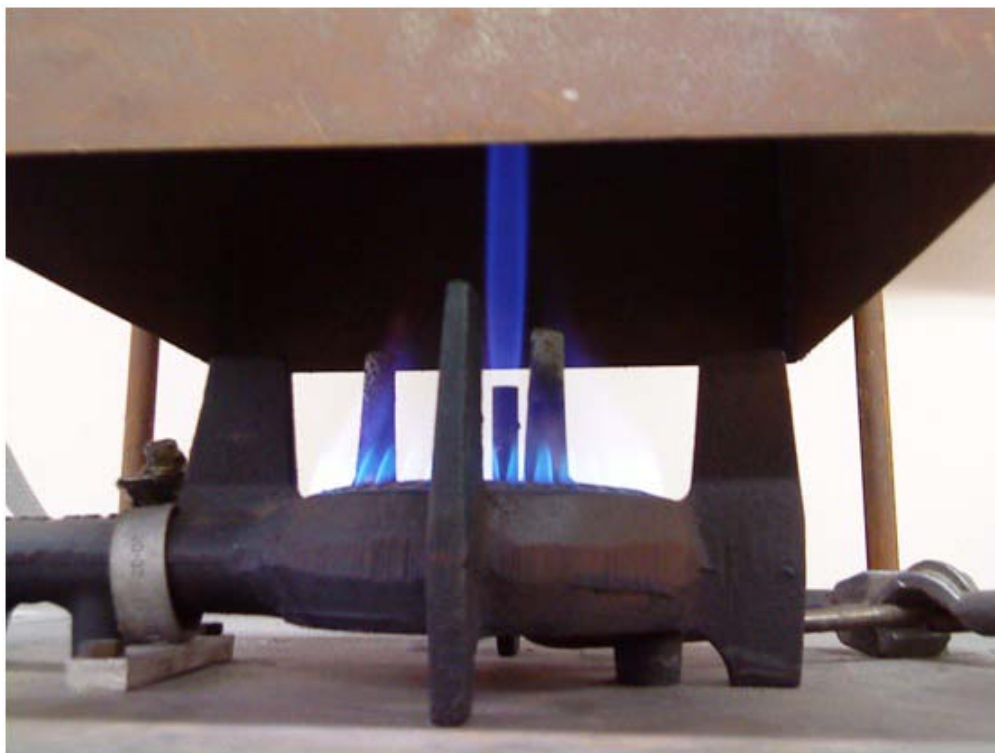


Figure 8: Gas incinerator: Auxiliary propane burner with fuel gas flame in the middle.

3.1.5 Gas Supply, Pressure Control and Measuring of the Volumetric Gas Flow Rates.

Pure CO_2 , N_2 , 20% O_2/CO_2 and air are supplied at 30 bar from gas cylinders and mixed at the desired flow rate and composition using two computer-controlled mass flow controllers (0 - 5 l/min CO_2 and 0 - 15 l/min CO_2 , Smart Mass Flow Controller, Brooks Instruments and 0154 Read out and Control Electronics, Brooks Instruments). The pressure in the reactor can be adjusted using a pressure let down valve (adjustable needle valve) placed after the gas cleaning traps/filters. By changing the pressure drop through the valve the system can be pressurised to any pressure up to the supply pressure of 30 bar. During an experiment the pressure let down valve is constantly adjusted manually as the volume of gas leaving the reactor is changing. This is because of changes in the extent of gasification and therefore the amount of gas produced during start up. Two pressure transducers (upstream and downstream of the reactor) are used to monitor the maximum pressure and the pressure drop through the reactor. An over pressure relief valve upstream of the reactor is set to 5 bar above the

desired reactor pressure. It is vented via a ¼ inch steel tube directly into the fume extraction hood. Testing showed that it is possible to safely depressurise the reactor through that valve. The volume of the fuel gas is measured with an installed dry gas meter (details: 3.2.1.1).

3.1.6 Steam Generator and Gas Preheater

Steam is generated by pumping deionised water with a metering pump (CM-4000 HPLC pump, LDC/Milton Bay) into a heated 1 in (i.d.) tube. Initial tests showed that all the water for flow rates 0 – 4 ml/min is immediately evaporated. A preheated side stream of the fluidising gas is used to carry the steam from the generator tube into the spout injection line where it is mixed with the remaining fluidising gas and the fuel before injection into the reactor. The generator tube is heated to 400°C using heating tapes. To prevent the steam from condensing downstream of the generator, the gas before the steam injection point is preheated to 400°C, as well as the tubing into the reactor. All parts are heated using temperature controlled heating tapes (3 x 400 W, 120 V, FGS051-060, Omega Engineering).

3.1.7 Resistance Heater, Temperature Control and Data Acquisition

The resistance heater for the reactor, temperature controller, pressure monitoring, mass flow controllers, online gas analysis and data acquisition were updated for this project and integrated in a single computer control/data acquisition program. Modification to the resistance heater and design of the temperature controller are outlined below. Two USB interfaces (RedLab 1008, Meilhaus Electronic GmbH and USB-TC, Measurement Computing) and LabVIEW² were used to develop the control for equipment and to log the data.

The reactor shell is resistance heated. Electrical power for heating is supplied from a high-output transformer (3 kW, 1.5 V) to two copper electrodes. The copper electrodes are split, with a semi-circular whole cut in each half. The two halves were bolted together around the top of the reactor holding the reactor in place. The bottom electrode floats to allow for the thermal expansion of the reactor body. During initial testing it was noticed that the injected coal was rapidly heated up in the spout line and

² LabVIEW 8.2.1, National Instruments

swelling led to frequent blockages. Therefore the extent of gas/coal preheating had to be decreased by reducing the length of the heated section of the reactor body. Raising the bottom electrode, however, decreased the resistance and increased the current through the system. This led to malfunctioning of the main transformer. To compensate for the decrease in resistance, the input voltage had to be regulated. A variable transformer³ between the wall socket and the fixed step down transformer was found to be the most suitable solution. The new setup allows varying the position of the bottom electrode, while keeping the power constant. A schematic diagram of the old and new set up is shown in Appendix B.2, page 245). Further modifications to the resistance heater included the redesign of the floating bottom electrode and the design of a water cooler for the cable connection between the bottom electrode and the transformer. Both modifications were necessary as the cables were heated up by conduction from the reactor and the cable insulation melted. This problem was more serious for the current project as operating under oxy-fuel conditions required a higher power input from the transformer. This is mainly because of the high heat capacity of CO₂ and the energy required for the endothermic char-CO₂ reaction.

For all temperature measurements 'K'-Type thermocouples with a stainless steel shaft and a maximum operating temperature of 1100°C are used. The temperature in the reactor can be measured at three different points: spout, bed middle and top of the bed. This was done for a number of runs to investigate the temperature distribution. For the majority of the experiments a single 3 mm thermocouple was used to measure the bed temperature. In addition gas inlet temperature and gas temperature after gas cooling were measured. The reactor body temperature was measured in the central part of the heated section. This temperature measurement is extremely important for the reliable operation of the reactor. Therefore the correct position of the thermocouple was checked before each run. To prevent the power supply from overheating, two thermocouples were placed in the fixed step down transformer (see Appendix B.2, page 245). The temperature was constantly monitored and the experiment was stopped immediately if the temperature exceeded 60°C, as it would indicate serious malfunction in the resistance heater.

³ 1 phase variable output transformer, 240V, 28A max., Carroll & Mynell Transformer Limited

A software based temperature controller was developed for this project. The key component was a proportional controller. The offset produced by the proportional controller could be eliminated very easily by using an integral part, but tests have shown that this would introduce instability due to integral wind-up. The input temperature for the controller can be selected from the wall temperature and the three bed temperatures. In case wall temperature is not controlled directly, penalty functions are activated to prevent the wall temperature of exceeding 1000°C. The characteristics of the control path are changed during the experiments and from one experiment to another. This is because of changing experimental conditions and changing characteristics of the resistance heater with temperature and time. Increasing resistance with increasing temperature is compensated using gain scheduling during the heating up period, while increasing resistance, due to high temperature oxidation of electrodes and cables, was compensated by adjusting the controller variables.

3.1.8 Flow Sheet

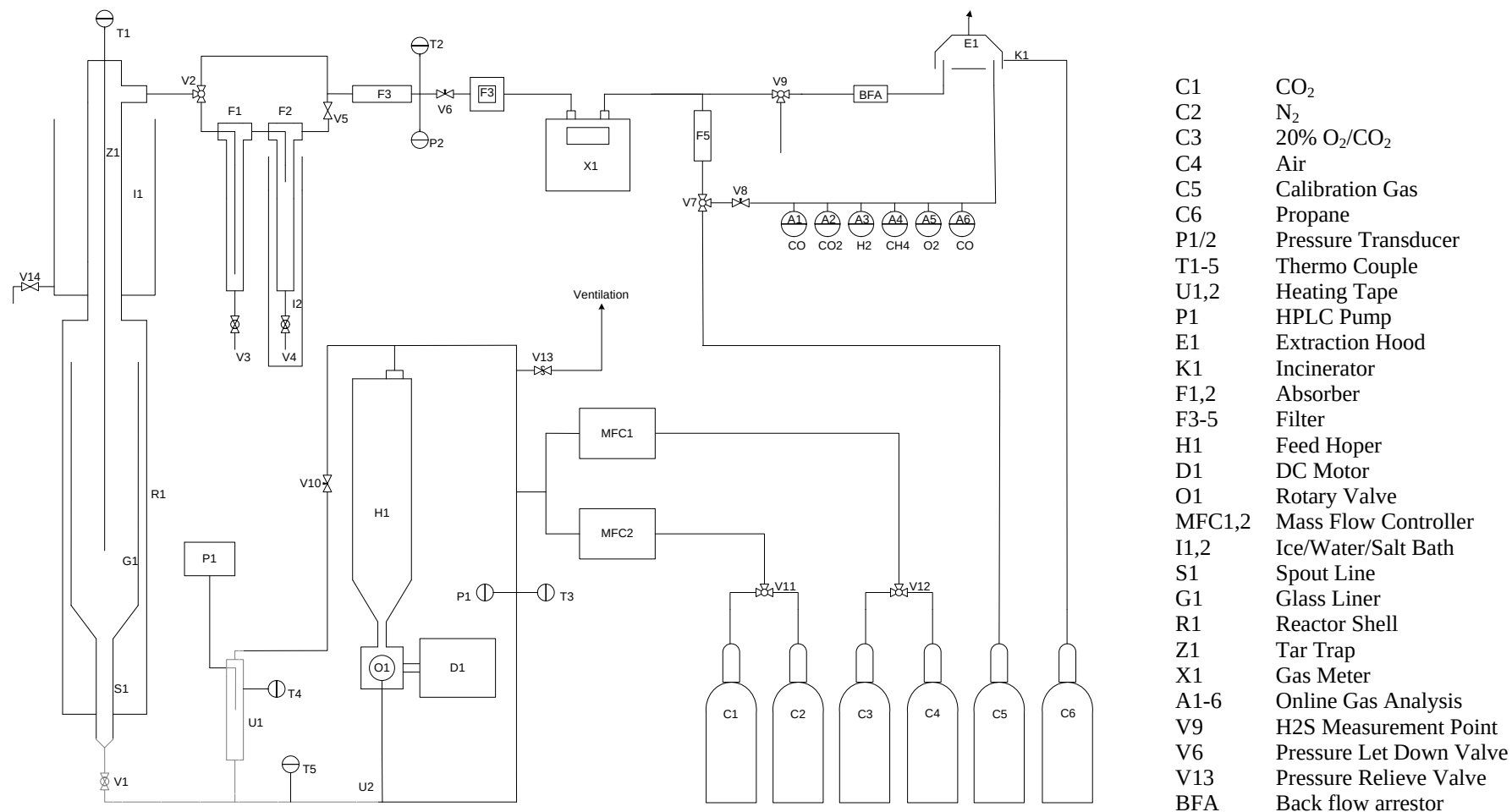


Figure 9: Flow sheet of the continuous fed high pressure fluidised bed rig

3.2 Analytical Methods

3.2.1 Fuel Gas analysis

3.2.1.1 Volumetric Flow Rate

The volumetric flow rate of the fuel gas is measured using a dry gas meter (Model G6, Meters UK Ltd). Measurements are taken every 2-3 min. For flow rates > 2 l/min, it was found that the reading on the dry gas meter varies from values measured with a bubble column. Therefore a calibration curve was determined and the measured values corrected. Data for the calibration can be found in Appendix A.1, page 241.

3.2.1.2 Major Components: CO₂, CO, H₂, CH₄

Table 4 shows the type, model, range and accuracy of the online gas analysers used in this project. The analysers were calibrated before each run using a certified calibration gas (certified gas mixture 1% CH₄, 15% CO, 15% CO₂, 10% H₂, balance N₂, accuracy $\pm 2\%$ of measured value and 100% CO₂ for the second calibration point, provided by BOC Ltd). The output signals of the analysers (0-5 V Servomex, 4-20 mA ADC and Hitech) are recorded using an AD converter with 12 bit resolution (see 3.1.7). The paramagnetic O₂ analyser and the second CO (0-25%) analyser were disconnected during the project as the O₂ concentration in the fuel gas was always zero and CO concentrations exceeded 25%. During calibration of the analyser the output signal in millivolt is recorded for each calibration point therefore it is possible to convert the measured signal in volume percentage (see 3.4.3.2).

The hydrogen analyser for this project was calibrated to measure up to 20% H₂ in CO₂. According to the information given by the supplier light hydrocarbons in the gas stream influence the measurement (no influence by CO). The only hydrocarbon present in a significant amount is CH₄. The data provided by the supplier⁴ showed that for 1% of CH₄, the error in the measured H₂ value was 0.08% (abs.). In most cases, the concentration of CH₄ in the fuel gas did not exceed 2 - 3% giving a maximum error of 0.24% (abs.) in the H₂ measurement. This was seen as not significant. For some experimental conditions the H₂ concentration in the fuel gas exceeded 20%. As the analyser continues to deliver measurement above 20% of H₂ and in absence of any other means of measuring H₂, linear

⁴ Hitech Instruments Ltd, 20 Titan Court, Laporte Way, Luton, England, LU4 8EF

behaviour of the analyser is assumed and the values were recorded. No measurement of H_2 in gas streams containing N_2 are possible using the current calibration because of the differences in thermal conductivity of CO_2 and N_2 . To estimate the H_2 content of the fuel gas under N_2 or O_2/N_2 blown conditions, a calibration curve of H_2 in N_2 was recorded. It shows almost linear behaviour in the range 0 - 20% H_2/N_2 (Appendix A.2, page 242). The values recorded by the analyser during these experiments are corrected according to the calibration curve.

Table 4: Online gas analysers – specification

Gas	Type	Model	Range	Accuracy	Comments
CO_2	Infrared	Servomex xentra 4200	0 – 100 %	+/- 1 % of measured value	
CO (I)	Infrared	see CO_2	0 – 25 %	see CO_2	
O_2	Paramagnetic	see CO_2	0 – 25 %	see CO_2	Calibrated using air
CH_4	Infrared	ADC	0 – 20 %	see CO_2	
CO (II)	Infrared	ADC	0 – 60 %	see CO_2	
H_2	Thermal Conductivity	Hitech K1500	0 – 20 %	see CO_2	Only H_2 in CO_2

3.2.1.3 Minor Components

3.2.1.3.1 Ammonia

The NH_3 concentration in the fuel gas is measured by absorbing into DI water and measuring the concentration of NH_4^+ using an ion selective electrode (ISE), Model: JENCONS-PLS, combination ion selective pH electrode. Water released from the reactor is condensed in the tar trap, which then absorbs the majority of the NH_3 in the fuel gas. Therefore NH_3 is collected during the whole length of the experiment and cannot be measured during the steady state period only.

After an experiment, the tar trap, the water bubbler and the steam trap are washed with DI water (analytical grade). The collected solution is filtered to remove fines and stored in a 1 l volumetric flask. The concentration of a constantly stirred 100 ml sample is then measured using the ISE connected to a pH-meter (4330 Conductivity & pH Meter, Jenway). The

position of the ISE, the volume of the sample and the stirrer speed of the magnetic stirrer are kept constant for all tests. The measured value is recorded after a 5 min period. The electrode is calibrated using 100 ppm, 1000 ppm 10000 ppm solutions prepared by diluting a standard NH_4^+ solution (0.1 M volumetric ammonium thiocyanate solution, Fisher Scientific). A new calibration curve is recorded for each batch of measurements. The calibration data for each batch of samples can be found in Appendix A.3, page 243. If the NH_4^+ concentration in the sample exceeded 10,000 ppm, it was further diluted until it was in the range of the calibration. Samples collected after experiments were not stored for more than 5 days before being analysed. Solutions of 2 different experiments were measured over a period of 14 days, with no significant change in the measured NH_4^+ concentration, indicating that they are reasonable stable. Separate measurements of the water collected from the tar trap and the bubbler showed that 95% of the NH_3 was absorbed in the tar trap, proving that NH_3 was successfully removed from the fuel gas and measured.

3.2.1.3.2 Hydrogen Sulphide

The H_2S content of the fuel gas is measured using Draeger-Tubes[®]. These are glass tubes filled with a chemical reagent that reacts to a specific chemical substances. A 100 ml sample of sample gas is drawn through the tube using a Draeger accuro[®] pump. The reagent in the tube changes colour and the length of the colour change indicates the measured concentration. In this work Draeger tubes[®] 100/a with a range of 100 - 2000 ppm for H_2S were used (standard deviation +/- 10% of the recorded value [148]). Markers on the tube for the measured concentration are given at 100, 200, 400, 600, ... , 2000 ppm. If the measured value was close to a scale mark, it's value was taken as the measurement. If the value lay between 2 markers, the mean value was recorded. Estimated error of the reading: +/- 50 ppm (combination of reading error and manufacturer's standard deviation).

Test were carried out to confirm that bubbling the fuel gas through water, to strip out NH_3 as described in 3.2.1.3.1, was not affecting the H_2S measurement. To judge the accuracy of the measurement, for a number of experiments several readings were taken during each experiment at steady state. Every time the same value was recoded in the error range described above.

3.2.1.3.3 Tar

In order to determine the amount of tar released during the gasification process all parts of the reactor, which were exposed to tar, were washed with a mixture of 400 ml chloroform/methanol (4:1 by volume). The solution was subsequently filtered to remove any fine particles. A rotary evaporator was used to evaporate the bulk of solvent at 60°C and atmospheric pressure. As soon as the volume was smaller than 50 ml, the solution was transferred to a pre weighed 50 ml glass jar. The jar was placed in a recirculating air oven overnight at 45°C to evaporate the remaining solvent. After that, the open jar was left for 2 h in laboratory atmosphere and the weight was recorded (Sartorius balance, 4 significant digits) every 30 min. For all experiments, the weight was constant after 2 h.

3.2.2 Thermogravimetric analysis

A thermo gravimetric analyser (Pyris 1 TGA, PerkinElmer) was used for non-isothermal char combustion reactivity analysis. The relative reactivity was determined by continuously measuring the sample weight loss while the sample was heated at a constant rate in an oxidising atmosphere. The char reactivity can be calculated using Equation 3.

$$R_{\max} = -\left(\frac{1}{W_0}\right)\left(\frac{dW}{dt}\right)\bigg|_{\max} \quad \text{Equation 3}$$

$R_{\max}$: maximum char reactivity

W_0 : initial weight of char sample, mg (daf)

dW / dt : rate of weight loss, obtained from the first derivative of weight loss curve

The following program was used:

- Switch gas to N₂
- Heat to 50°C at max heating rate
- Hold at 50°C for 5 min
- Heat to 400°C at 25°C/min
- Hold at 400°C for 30 min
- Switch to air
- Heat to 900°C at 25°C/min
- Hold at 900°C for 10 min

In all cases, sample mass was 2.5 mg $\pm$ 0.2 mg. Flow rates of nitrogen and air were held constant at 40 l/min.

3.2.3 Size Exclusion Chromatography (SEC)

NMP solutions of coal derived tar were analysed by size exclusion chromatography (SEC). A Mixed-D column from Polymer Laboratories packed with polystyrene/polydivinylbenzene was used in this work. The column was heated to 85°C. A 0.5 ml/min flow of NMP was pumped through the system. The signal was detected by ultraviolet absorption at wavelengths of 280, 300, 350 and 370 nm using a Diode Array detector. Software developed in this laboratory was applied to normalize intensities to allow comparison between runs.

3.2.4 UV Fluorescence Spectroscopy (UV-F)

A Perkin-Elmer LS55 Luminescence Spectrometer has been used in the static cell mode determination. Solutions of the samples in NMP have been measured at 240 nm/min between 330 and 800 nm. The spectra have been recorded in three different modes. For the emission spectrum the sample is excited at a constant wavelength and the emission is recorded in the full range of wavelengths. The excitation spectrum is recorded at a fixed wavelength, while the excitation frequency is changed over the range. In the synchronous spectrum, both excitation and emission are simultaneously varied, but the wavelength difference is 20 nm at any time.

3.2.5 Optical Microscopy and Electron Microscopy (EM)

For the optical analysis of the char surface, an optical microscope with a digital camera and an electron microscope (TM-1000 Hitachi Tabletop Microscope) have been used.

3.3 Fuel Samples Selection, Preparation and Analysis

3.3.1 Selection of Fuel Samples

Five different fuel samples have been used (see Table 6). Daw Mill Coal is a bituminous coal used in UK coal fired power plants. Coalite is a smokeless fuel, commercially available. Both were used in previous projects with the fluidised bed reactor and were used in this project for initial testing and comparison. Feedstock samples provided by the Flexgas project partners include German lignite, Polish coal and Italian olive bagasse. These fuels are available in large quantities and are candidate fuels for future power generation in Europe. Low rank coals, like the German lignite, are the preferred option for fluidised bed gasification due to their high reactivity. The higher rank Polish coal was chosen to explore the possibilities of extending the range of possible feedstock. Olive bagasse is a waste product from the olive oil production. Its utilisation as a fuel for power generation would combine waste reduction and reduction of carbon dioxide emissions.

3.3.2 Preparation

As described in 3.1.3, the fuel feeding system requires a narrow particle size distribution of 200 - 300 μm . All fuel samples were received with a top size of 3 mm making it necessary to crush and grade the fuel before use. Daw Mill coal and Coalite were ground using a swinging hammer mill with an integral 1 mm screen. The fuel was then sieved for 3 hours to obtain the sample in the required size fraction of 200 - 300 μm . This method turned out to be extremely time consuming and not suitable for preparing the required amounts of fuel for the project. The main problem was the limited throughput of the lab scale hammer mill. The preparation of the other fuels was therefore carried out at the Central Support Laboratories of RWE ⁵. The equipment used is shown in Figure 10. Table 5 shows the preparation procedure and the final yield for each fuel. Only Polish coal could not be prepared as received, as it was too wet to crush and had to be pre dried. The prepared samples were stored in closed containers under a nitrogen atmosphere.

⁵ Central Support Laboratories, RWE Power International, Drax Business Park, Selby, North Yorkshire, YO8 8PO

Table 5: Preparation procedure for different fuels

German Lignite	Top size: 3 mm Olive Bagasse	Polish Coal
↓		↓
Hammer Mill		
↓	↓	Drying: 48 h, 30°C
Grading*	Disc Mill	↓
↓	↓	Hammer Mill
Disc Mill	Grading*	↓
↓	↓	Grading*
Grading*		↓
↓		
10 kg	2 kg	2 kg
Size Range: 200 - 300 µm		

*Sample > 300 µm was crushed again, sample < 200 µm was removed. This process was repeated twice



Figure 10: Equipment used for fuel preparation in the Central Support Laboratories of RWE. From the left: 50 cm sieves for grading; hammer mill; 11" disc mill; fuel drying oven.

3.3.3 Analysis

Proximate, ultimate, ash constituents and ash fusion temperature analyses of the fuels were provided by a commercial analytical laboratory⁶ and by Flexgas project partners. Table 6 shows the results based on “as received” basis.

Table 6: Feedstock Analysis

Sample	Daw Mill Coal	Coalite	Olive Bagasse	German Lignite	Polish Coal	
Treatment					dried ³	
Original Supplier	UK IC	UK IC	Italy Flexgas	Germany Flexgas	Poland Flexgas	
Type	bituminous coal	smokeless fuel	residual biomass	brown coal	bituminous coal	
Prox. analy. ¹						
Moisture %	5.0	5.0	3.7	13.2	13.3	3.2
Ash %	8.8	3.7	5.2	4.1	7.7	6.2
Volatile Matter %	33.0	36.8	67.2	44.0	28.7	32.6
Fixed Car. % ²	53.2	54.5	23.9	38.7	50.3	58.0
Ulti. analy. ¹						
Sulphur %	1.61	0.46	0.06	0.23	0.33	0.41
Chlorine %	0.25	0.01	0.07	0.02	0.15	0.17
Carbon %	69.02	73.42	45.61	57.39	64.97	74.55
Hydrogen % ⁴	4.15	4.74	5.09	4.03	3.60	4.30
Nitrogen %	1.18	1.5	1.36	0.61	1.07	1.26
Oxygen % ^{4,6}	9.99	11.17	38.91	20.42	8.88	9.91
Oxides in Ash, % by mass			5	5	5	
SiO ₂	46.0	62.8	15.7	3.1	29.6	
Al ₂ O ₃	21.7	18.7	4.9	4.2	8.2	
CaO	7.2	2.3	17.8	49.5	24.2	
Fe ₂ O ₃	9.1	10.8	4.0	11.6	21.6	
K ₂ O	1.8	1.0	42.7	1.8	1.1	
Na ₂ O	0.8	0.6	1.2	6.7	2.3	
MgO	2.7	0.8	3.7	23.0	12.6	
P ₂ O ₅	0.5	0.6	10.1	0.1	0.3	
TiO ₂	0.9	0.8	n.a.	n.a.	n.a.	
Mn ₃ O ₄	0.2	<0.1	n.a.	n.a.	n.a.	
Ash Fusion Temp.						
Deformation [°C]	1210	1180	1200	1380	1190	
Softening [°C]	1220	1210	1230	1390	1200	
Hemisphere [°C]	1230	1290	1230	1400	1210	
Flow [°C]	1240	1370	1330	1490	1220	
Swelling Number	0.0	0.0	0.0	0.0	0.5	

¹ ‘As received’ basis

² By difference

³ Sample dried for 48 hours at 30°C

⁴ Corrected for moisture

⁵ Provided by Flexgas partner

⁶ by difference

⁶ TES Bretby, Burton-on-Trent, Staffordshire, DE15 0XD, UK

3.4 Procedures

3.4.1 Introduction

First, the procedures for carrying out experiments under atmospheric pressure and elevated pressure are described, together with the procedure for emergency shut down in case of malfunctioning. The experimental test procedure, the data analysis and the calculations based on the measured data are then described in detail.

3.4.2 Experimental

3.4.2.1 Experiments under Atmospheric Pressure

- A feedstock sample (typically 60 g) is weighed (Sartorius VC-711 balance, 1 significant figure) and placed in the hopper. Depending on the scope of the experiment, the sample weight can be between 2 and 60 g. The hopper is sealed and connected to the pressurised gas supply
- The quartz glass liner is placed on the spout and inserted in the reactor shell. Several pieces of quartz paper are used as a seal between the spout line and the glass liner. The bottom flange is closed. The counter weight is placed on top of the gas liner and the top flange is closed.
- A constant flow of 2 l/min CO₂ is set on the mass flow controller.
- 60 g of initial bed material is filled into the reactor and immediately fluidised by the flow of CO₂.
- The tar trap is placed on top of the reactor and the outlet is connected to the downstream equipment: filters, flow meter, gas meter, online gas analysis and ventilation. The tar trap is filled with ice, water and 20 g of salt.
- The rig is pressurised to about 5 bar_g using the pressure let down valve downstream. The pipework and the reactor is tested for leaks.
- After all connections are sealed, the reactor is depressurised to near atmospheric pressure (any pressure build up is a result of the pressure drop through the equipment, typically 0.3 bar) and the reactor wall is heated up to 50°C above the desired reaction temperature.
- During this heating up period, the analysers are calibrated.

- Shortly before the required temperature is reached, the desired mixture of O_2/CO_2 is set on the mass flow controllers, the auxiliary burner for the gas incinerator is lit and the CO leak alarm is activated.
- As soon as the wall temperature and bed temperature are stable, the feeding motor and the feed hopper vibrator are started.
- An immediate drop in bed temperature and a small increase in the pressure drop through the reactor (typically 0.2 bar) indicated beginning of feeding and the parameters of the temperature controller are constantly adjusted to keep the average bed temperature at the desired value. If the bed temperature does not drop during the first 5 min, no fuel is fed to the reactor and the run is aborted. If the pressure drop through the reactor increases further during the run, the test is stopped as this indicated blockage in the spout line.
- During the run, exit gas temperature is monitored and kept below room temperature by draining warm water from the bottom of the tar trap and replacing ice and salt.
- As soon as the feed hopper was empty and no fuel was fed in the bed, the bed temperature increased sharply. The power supply for the heater is switched off and the gas supply is switched back to 2 l/min of 100% CO_2 .
- The bed is left to cool down to approximately 50°C (approximately 2.5 hours) before the valve downstream of the reactor is closed and the fluidising gas is switched off.
- The reactor is taken apart, the bed material is recovered and the reactor and tar trap are washed for subsequent tar and NH_3 analysis (see 3.2.1.3).

3.4.2.2 Experiments under Elevated Pressure

- The cold reactor is leak tested at a pressure 5 bar above the desired working pressure.
- The wall temperature is set at the maximum allowable value.
- During the heating up period the gas flow rate is increased in steps to the desired value. At the same time the pressure in the reactor is adjusted to a value 3 bar below the desired working pressure. This is necessary to compensate for the rapid increase in pressure as soon as the fuel feed rate is increased (which increases the gas flow rate).
- As soon as the fuel hopper is empty the reactor is depressurised by step wise decreasing the flow rate to 2 l/min and gradually opening the pressure let down valve.

3.4.2.3 Experiments with Steam Injection

- During reactor heating up, the gas preheating and the steam generator are heated to 400°C. At stable operating conditions (pressure, temperature) the HPLC pump is set to the desired value and switched on and the system is left for 5 min to stabilise. Initial testing showed that after 5 min a constant flow of steam is generated and all the water supplied by the pump is immediately evaporated.
- The steam generator is switched off immediately after the fuel feeding is finished.
- The tar trap is removed before the gas supply to the bed is switched off. This was found to be necessary to prevent quantities of condensed water dropping from the tar trap back into the reactor.

3.4.2.4 Rapid Shut-Down Procedure

The sequence of shutting down equipment in case an experiment had to be aborted immediately is as follows:

- Reduce gas flow rate to 2 l/min. As this means the flow rate is reduced to 1/8 compared to the flow rate used for 20 bar, the pressure in the reactor is decreased rapidly. It was found that keeping the bed fluidised with a small flow of gas was in most cases better than interrupting gas flow and allowing the hot solids from the bed to enter upstream parts of the equipment.
- Stop the supply of oxygen to the reactor.
- Switch off resistance heater
- Switch off gas pre heater and steam generator
- Switch off fuel feeder
- Slowly open pressure let down valve.

Rapid pressure release by fully opening the pressure let down valve had to be avoided, as downstream equipment only could withstand up to 5 bar pressure. Pressure release via the pressure relief valve resulted in safe, but rapid release of hot particles and large quantities of combustible gas into the ventilation duct. Due to the damage to the equipment (the tubing and valve between the reactor and the safety valve have to be replaced) caused by this, it was only seen as an emergency option.

3.4.3 Analysis of the Results

3.4.3.1 Introduction

A MATLAB⁷ program is used after the experiment to analyse the results. The duration of the experiments was less than 1 hour, therefore measured and calculated values for each experiment are given as ‘per min’ where appropriate. For the calculations ideal gas behaviour is assumed with 22.4 l as molar volume under standard conditions (Standard Conditions). For each experiment, fuel gas composition, fuel gas flow rate and solid fuel feeding rate were measured. Based on these data, carbon conversion and heating value of the fuel gas can be calculated. The methods to analyse the data are described in detail below.

3.4.3.2 Fuel Gas Composition

As the fuel gas from the gasifier is cooled to room temperature, all water is condensed and the composition of the dry fuel gas is measured. Therefore fuel gas compositions in this work are given on dry basis unless stated otherwise. In order to estimate the water content of the hot fuel gas it is assumed that hydrogen from the solid fuel is released as H₂, CH₄ and H₂O, therefore the amount of steam in the gas can be calculated using hydrogen balance with steam content in the hot fuel gas as variable:

$$H_{in}(\text{fuel moisture, steam, fuel hydrogen}) = H_{out}(\text{fuel gas : H}_2, \text{CH}_4, \text{H}_2\text{O})$$

This assumes that there is no H remaining in the bed char and no significant tar release. It has to be noted that the first assumption is only valid for higher ranked coals. For low ranked coals and biomass, the bed char can contain a significant amount of hydrogen. Because of the potential large error the calculated values are only used to establish general trends.

Figure 11 shows the recorded values of the fuel gas composition (CO, H₂, CH₄ and CO₂) during a sample experiment. The start up period and the reaching of steady state are discussed in more detail in section 3.5.4, page 106. Using the calibration carried out before each experiment (see 3.2.1.2) and the recorded millivolts signal during the calibration, the signal is converted into a value for the volume percentage of each component. The fuel gas composition is measured by taking the average value for each gas during the steady state period. In the example shown in Figure 11 this would be from t = 20 min until the end of the

⁷ MATLAB 7.0, The MathWorks, Inc.

experiment. It is assumed that the 4 measured gases account for 100% of the measured fuel gas. However because of experimental errors (see 3.5.3) the summation of the measured values does not add up to exact 100% (in the example: 102.1%), therefore the values are normalised to 100%.

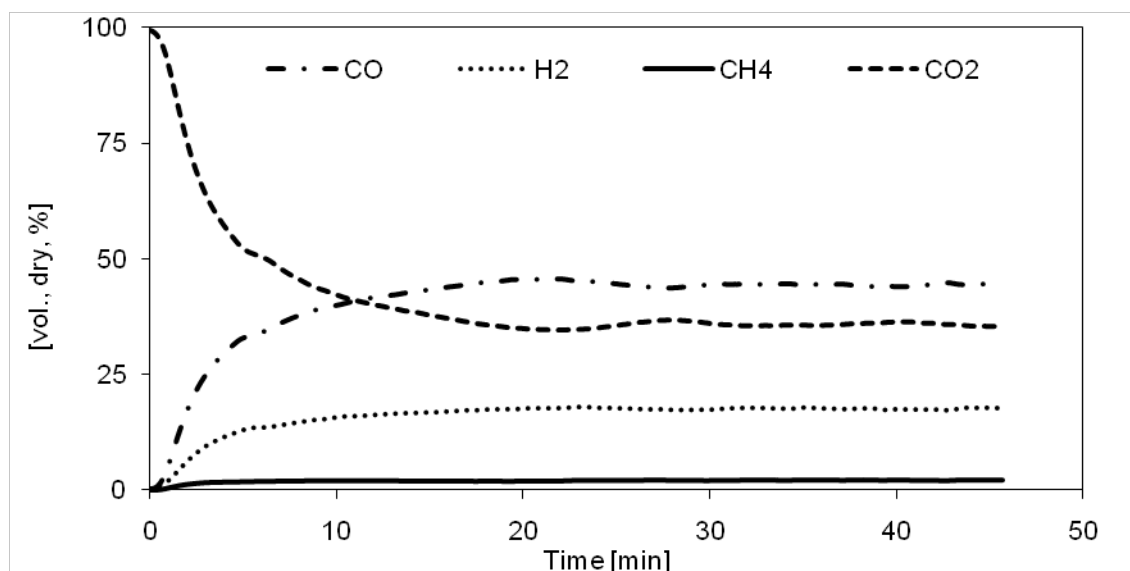


Figure 11: Normalised fuel gas composition during continuous gasification of GL. Start up and steady state operation (feed rate: 1.7 g/min) in high CO₂ atmosphere (90% CO₂ and 10% O₂) at 850°C and atmospheric pressure.

3.4.3.3 Volumetric Fuel Gas Flow Rate

The volumetric flow rate of the fuel gas is measured using a dry gas meter (see 3.2.1.1, page 82). In addition, the volumetric flow rate can be approximated using an oxygen balance. For that it is assumed that the number of mols of oxygen entering the reactor is equal the number of mols of oxygen leaving the reactor:

$$O_{in}(CO_2, O_2, \text{pyrolysis product} : CO_2, CO) = O_{out}(\text{fuel gas} : CO_2, CO)$$

Note: Any O₂ released as H₂O is not accounted for.

The amount of oxygen entering in the fluidising gas is controlled by the mass flow controllers. Separate experiments are carried out for each condition (temperature and pressure) to estimate how much oxygen is released during pyrolysis. The fuel gas composition is measured with the online gas analysers. The volumetric flow rate of the fuel gas can be calculated by iterative methods, which do not include oxygen leaving the reactor

as water and tar. Figure 12 shows the comparison between the measured values for the volumetric flow rate using the dry gas meter and the calculated values using the oxygen balance. It can be seen that there is a very good agreement between the two methods. The difference and the associated error and its implication are discussed in 3.5.3, page 102.

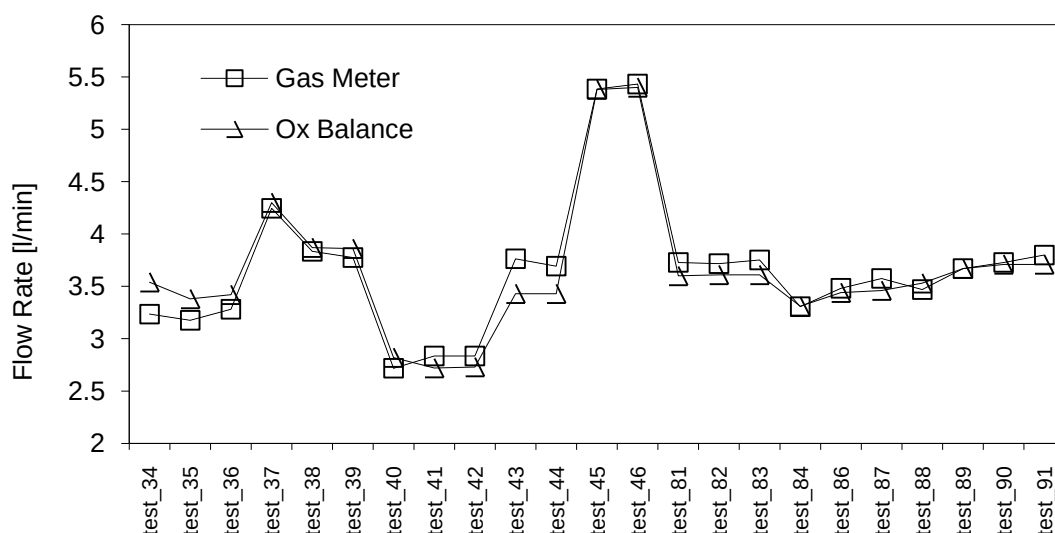


Figure 12: Comparison of the volumetric flow rate measured by dry gas meter and calculated by oxygen balance.

3.4.3.4 Solid Fuel Feed Rate

The feed rate of solid fuel into the reactor is assumed to be constant during the duration of the experiment. The total amount of fuel injected is calculated from the weight of fuel in the hopper before and after the experiment. The duration of the fuel injection is calculated by measuring the time CH_4 is released (from the point where CH_4 is first recorded until the point where the CH_4 concentration sharply decreases) as the CH_4 mainly is produced during pyrolysis and its release is directly connected to the fuel injection. The stability of the CH_4 reading can be therefore used to judge the stability of fuel feeding.

3.4.3.5 Carbon Conversion

Carbon conversion (X) is calculated from the fuel gas analysis and the fuel feeding rate (Equation 4 and Equation 5). Determination of carbon conversion based on the remaining carbon in the ash is not possible with this experimental set up as no solid material is removed from the reactor during the process. The material recovered after the experiment contains

carbon accumulated during start up and therefore does not correspond to the unconverted carbon during steady state operation alone.

$$X = \frac{\text{Mole of Carbon in Fuel Gas} - \text{Mole of Carbon in Fluidising Gas}}{\text{Mole of Carbon in Coal}} \quad \text{Equation 4}$$

$$X = \frac{100 \cdot 12}{22.4} \frac{(x_{CO} + x_{CO_2} + x_{CH_4})F - F_{CO_2}}{FFR \cdot x_{C-coal}} \quad \text{Equation 5}$$

n : CO, CO₂, CH₄

x_n : Mole fraction (= volume fraction)

F : Fuel gas flow rate [l/min] (standard conditions)

F_{CO_2} : Flow rate CO₂ in the reactor [l/min] (standard conditions)

FFR : Fuel feeding rate [g/min]

x_{C-coal} : Mass fraction of carbon in the coal

3.4.3.6 Heating Value

In this project the lower heating values (LHV or net calorific value) for the fuel gas and for the solid fuels are calculated. The calculation of the LHV assumes all combustion products are in the vapour phase after combustion. Therefore, the enthalpy of vaporisation of water in the reaction product is not recovered. The higher heating value (HHV or gross calorific value) includes the enthalpy of vaporisation. Table 7 gives the heating value for the components in the fuel gas. The LHV for the measured fuel gas composition under standard conditions is calculated as follows:

$$LHV_{gas} [\text{MJ/m}^3] = \sum_n 22.4^{-1} \frac{\text{kmol}}{\text{m}^3} 10^3 x_n LHV_n \quad \text{Equation 6}$$

n : CH₄, H₂, CO

x : Mole fraction (= volume fraction)

LHV_n : Heating value [kJ/mol]

Table 7: Heating value (LHV) of fuel gas components.

Gas	Heating Value (LHV)	Reaction
CH ₄	803 kJ/mol [149]	CH _{4(g)} + 2O _{2(g)} ⇌ CO _{2(g)} + 2H ₂ O _(g)
H ₂	242 kJ/mol [7]	H _{2(g)} + ½ O _{2(g)} ⇌ H ₂ O _(g)
CO	283 kJ/mol [7]	CO _(g) + ½ O _{2(g)} ⇌ CO _{2(g)}

The lower heating values for the solid fuels are estimated using Equation 7 [149] where C, H, S, A, O and N are the weight percentages on dry basis of carbon, hydrogen sulphur, ash, oxygen and nitrogen, respectively.

Table 8 lists the estimated heating values of the solid fuel.

$$LHV_{fuel} [\text{kJ/g}] = 0.341C + 1.323H + 0.685S - 0.015A - 0.120(O + N) \quad \text{Equation 7}$$

Table 8: Estimated heating value of the solid fuels.

Fuel	LHV [kJ/g]
Daw Mill Coal	29.08
German Lignite	25.72
Polish Coal	30.66
Olive Bagasse	18.04

Based on the heating value of the fuel gas and the solid fuel the energy conversion can be calculated using Equation 8.

$$\text{Energy Conversion } [\%] = 100 \frac{F \cdot LHV_{gas}}{FFR \cdot LHV_{fuel}} \quad \text{Equation 8}$$

F : Gas flow rate (standard conditions)

FFR : Fuel feeding rate

3.5 Commissioning of the Experimental Set Up

3.5.1 Introduction

The commissioning of the experimental set up is divided into 3 sections. Section 1 deals with the fluidising behaviour of the reactor. The main purpose is to show that there is a sufficient degree of solid back mixing in the bed. In section 2, the errors of the measurements and their implications on the repeatability of the experiment are discussed. In Section 3, the fuel gas composition during an experiment is analysed in more detail, the focus is on the fact that a steady gas composition is reached in each experiment.

3.5.2 Fluidising Characteristics

3.5.2.1 Introduction

For this project the selection of the superficial velocity was constrained by the requirement of the gasification conditions and limitations of the equipment. Flow rate, feed rate, gas residence time, O/C ratio and CO₂/C ratio are dependent variables, leaving only a limited range in which the superficial velocity can be adjusted. The optimal flow regime for the reactor would enable:

- Back mixing of solids
- Minimum amount of entrained particles in the fuel gas stream
- Homogeneous bed temperature/high rate of heat transfer from the reactor wall
- High enough spout velocity to ensure pneumatic transport of solids in the tubes and injection into the bed

Previous studies [63] carried out with this reactor used four times the minimum fluidising velocity as a value for the superficial gas velocity (u_s), as is commonly applied for fluidised bed reactors [17, 23, 150]. For this project, a set of tests and calculations were carried out to assess the fluidising properties using different gas velocities and to establish the optimal experimental conditions.

3.5.2.2 Assessing Fluidising Behaviour

Firstly the minimum fluidising velocities for different particle sizes and densities in the reactor were calculated and compared (A). Secondly, the results from cold testing are discussed (B) and thirdly the temperature distribution in the bed (hot testing) is measured (C).

A) The superficial velocity for a gas flow rate of 2 l/min⁸ and the calculated minimum fluidising velocities (calculation given in Appendix C.1, page 246) for different temperatures and different particle sizes are shown in Table 9. The following points are observed: (1) Range for u_{mf} is: 0.012 – 0.54 m/s (2) Difference in u_{mf} for different particles is larger than for different operating conditions (temperatures). (3) Resulting u_s always higher than four times the minimum fluidising velocities. It can be concluded that based on these calculations it would be feasible to use a volumetric flow rate of 2 l/min for experiments under atmospheric pressure, over the whole range of possible temperatures.

Table 9: Fluidising Velocities

		700°C			800°C			900°C		
	d_p [μm]	U_s [m/s]	U_{mf} [m/s]	4 x U_{mf} [m/s]	U_s [m/s]	U_{mf} [m/s]	4 x U_{mf} [m/s]	U_s [m/s]	U_{mf} [m/s]	4 x U_{mf} [m/s]
Char	100	0.18	0.012	0.048	0.2	0.013	0.05	0.22	0.013	0.053
	300	0.18	0.04	0.15	0.2	0.038	0.15	0.22	0.04	0.16
1400 kg/m³										
Sand	100	0.18	0.017	0.066	0.2	0.017	0.07	0.22	0.018	0.072
	300	0.18	0.05	0.2	0.2	0.052	0.21	0.22	0.054	0.22
2600 kg/m³										

1 Data for gas density and viscosity were taken from “Nist Chemistry WebBook [151]” and extrapolated where necessary.

2 Data for particle density were taken from [63].

3 u_s is based on a flow rate of 2 l/min

4 U_s and u_{mf} in m/s

5 d_p in μm

⁸ Initial testing of the reactor under atmospheric pressure was carried out at 2 l/min. Under these conditions the bed seemed to be properly fluidised and the gas velocity was high enough to transport and inject the fuel.

B) Cold tests were done to assess the mixing behaviour during fuel injection. Similar to the result of Cousins et al. [64], an initial sand bed weight of 60 g was found to give the best mixing behaviour as determined by visual observation. A gas flow rate of 2 l/min was used for this. In the bottom part of the bed, the gas jet from the central injection point created a submerged spout, where solids are entrained and carried upwards. Bed solids gradually slipped down the wall to be entrained in the spout jet and mixed with the fuel. In the top part of the bed the spout is broken up, and this section exhibits a bubbling fluidised bed behaviour. A tendency to slugging behaviour in the top part was observed under higher velocities as a result of the small reactor diameter. In the next step, the superficial velocity was varied from 0.05 m/s to 0.27 m/s⁹. A more rapid mixing of the injected solids was observed as the velocity increased between 0.05 m/s and 0.15 m/s, while no significant differences could be observed between 0.15 and 0.27 m/s. The continuously injected coal was observed to rapidly mix with the bed material under all tested conditions, while the back mixing of the bed seemed to improve while fuel was injected. Based on the observation from the cold tests, it can be concluded that the reactor could be operated under the whole range of tested superficial velocities with a sufficient rate of back mixing of bed solids and fast fuel injection/mixing.

C) The temperature distribution in the bed is used as means of assessing the degree of back mixing under different conditions. Temperature profiles of the fluidised sand bed (60 g) were measured along the height of the bed at 700°C, with N₂ as fluidising gas, for the whole range of gas velocities. From Figure 13 it can be seen that the main part of the sand bed is isothermal. Only a small section at the bottom of the bed had a slightly lower temperature probably due to the cooling effect of the incoming gas in this area. During cold tests, it was seen that the continuous injection of fuel affects the fluidising behaviour. To investigate this effect as well as those of the endothermic gasification reactions and the higher thermal capacity of CO₂ (compared to N₂) on the temperature profile of the bed, three thermocouples were used to measure the temperature at the bottom, middle and top section of the bed during an experiment. Figure 14 shows the measured bed temperatures during start up and during the continuous injection of fuel. It appears that there is a 100°C difference between each section during start-up probably due to the high thermal capacity of CO₂. The gas has to pass through the major part of the bed before it is heated to the desired temperature. As soon as the fuel

⁹ The calculated minimum fluidising velocity at 900°C for the sand is 0.018 m/s and for char particles 0.013 m/s

feed was switched on the temperature in the top section decreased due to the effect of endothermic gasification. However, it also seems that the solid injection improved the solid back mixing, as already mentioned, in the bed leading to an isothermal top and middle section and a 50°C cooler bottom section. These initial tests indicated good mixing of solids and isothermal bed conditions for the range of gas velocities investigated.

In addition to the test described above, the pressure drop through the bed was monitored (200 – 400 mbar). However no change in pressure drop with changing fluidising velocity could be observed.

3.5.2.3 Conclusion

It was concluded that there was no significant influence of the superficial velocity on the back mixing of solids and temperature distribution in the range investigated. A superficial velocity between 0.14 m/s and 0.18 m/s and was chosen for the majority of the experimental programme. The exact velocity is determined by the requirements of the experimental conditions (fuel feeding rate, O/C ratio, etc.) as mentioned above.

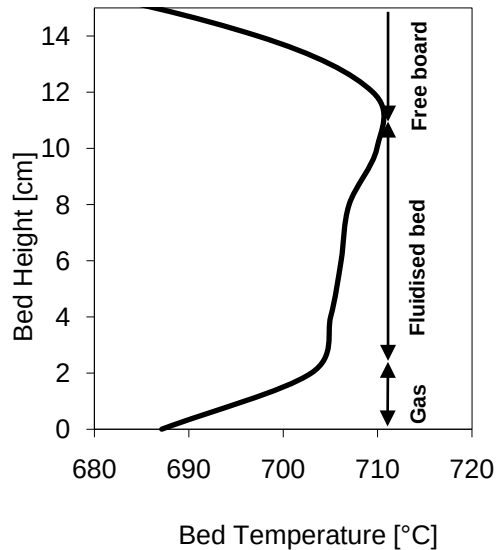


Figure 13: Temperature profile in the spouted bed, 700°C, 2 l/min N₂ gas flow rate

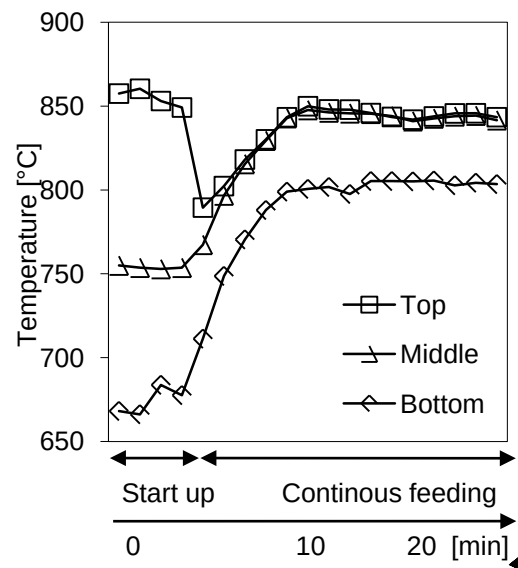


Figure 14: Bed temperature measured during solid feeding at 3 different positions: Top of the bed, middle section and bottom section

3.5.3 Repeatability and Measurement Errors

3.5.3.1 Introduction

To analyse the quality of the experimental results and to determine whether measured differences are sufficiently large to identify trends, overall errors for the fuel gas composition and the carbon conversion data have been calculated and compared with the repeatability of the data. The possible sources of experimental errors are identified, their maximum values are estimated and the impact of the errors on the measured results have been calculated and discussed. In the first part of this section errors associated with the measurement of the major fuel gas components and the related calculated values are discussed.

3.5.3.2 Sources and Extent of Errors

A known maximum error can be given for the following three measurements as these data are provided by the supplier:

- (1) Online gas analyser: The accuracy of the measurement is given with 1% of the measured value. It has to be noted that the stated error is only the error introduced by the measurement itself. The calibration of the analysers introduces further inaccuracy (discussed below) as well as the way the measurement is taken (see 3.4.3.2). Analysing the average difference between the summations of the percentage of measured gases (expected to be 100%) an overall error of 2.7% for the measured value can be calculated. The same maximum error can be expected after normalising the values as explained before.
- (2) Calibration gas: The accuracy of the mixture is given by the supplier as +/- 2% of the certified values. The maximum error for each measurement is given in Table 10. During the whole project, the same cylinder of calibration gas was used and therefore the influence on the measurement was the same for each experiment and therefore did not have an effect on the qualitative trends observed in this study.

Table 10: Maximum error of calibration gas and influence on measurement.

	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	Σ [%]
Value	15	15	10	1	
Error +/-	0.3	0.3	0.2	0.02	0.82

- (3) Mass flow controller: Given accuracy of 1%, but the accuracy was found to be limited by the computer control programme rather than the controller itself. For details see below.

For measurements where no error data are available from the manufacturer, a maximum error has to be estimated:

- (4) Volumetric flow rate of the fuel gas: An average error for the flow rate measurement can be estimated by comparing measured flow rates and by oxygen balance calculated flow rates. Taking the data from Figure 12 an average difference between the two flow rates is 0.12 l/min.
- (5) Control of the mass flow controller by a 0 - 5 V signal: The interface used to control the mass flow controller (see 3.1.5) has a theoretical resolution of 12 bit. Therefore it should be possible to achieve an accuracy of ± 1.2 mV on the output channels. This was, however, found not to be the case. In reality it was possible to control the flow with an accuracy of approx ± 0.05 l/min of the set point (compared to measurement by bubble column). Reasons for that are the limitation in the power supply of the interface and the length of the signal cables.
- (6) Solid fuel feeding rate: Two cases have to be distinguished: (1) Measuring the average feeding rate after each run. This is done by weighing the inventory of the fuel hopper before and after each experiment and by measuring the feeding time and is not associated with a significant error. (2) Setting the required feeding rate before each run by controlling the speed of the motor that drives the rotary valve. The motor speed can be adjusted by varying the supply voltage, which can be controlled accurately. However mechanical stress on the drive shaft caused by small movement of the rotary valve and friction caused by the seals of the rotary valve are found to affect the actual speed of the motor and cause variation in fuel feeding rate. The analysis of the repeatability of the feed rate from the results discussed in 3.5.3.4, show a variation of 6% from the set value. For higher feed rates this is like to increase and a variation of 10% can be assumed.

Pressure and temperature measurements are not directly used in the calculation of experimental results, however they do affect the gasifier performance:

- (7) Pressure transducer: The accuracy of the measurement is ± 0.1 bar. However the pressure in the reactor can only be controlled in a range of estimated ± 1.5 bar at a given set point for experiments at elevated pressure (Range: 5 – 20 bar). This was estimated by pressuring up the reactor to 10 bar and observing the variation over the course of 30 min. Experiments at elevated pressure are carried out at 5, 10, 15 and 20 bar, therefore the difference between each condition is larger than the maximum error.
- (8) Temperature measurement: Temperature is measured using 'K'-Type thermocouples with an accuracy of $\pm 4^{\circ}\text{C}$ at 1000°C [152] . During the design and testing of the temperature controller it was found that the temperature in the reactor can be controlled at a given set point with a estimated $\pm 25^{\circ}\text{C}$ accuracy at any given condition. The error comes from the very slow response time of the system, preventing a more accurate control. Similar to experiments at elevated pressure, experiments at different temperatures are carried out with large temperature increments of 100°C to ensure differences are larger than the maximum error.

3.5.3.3 Overall Error

In the previous section, the sources of errors have been discussed and maximum errors for each measurement established. Based on this data an overall error for carbon conversion can be estimated by calculating the linear error propagation. The linear error propagation calculates the worst possible error, assuming maximum error for each measurement and positive summation of the errors. The influence of the measurement errors on the final value for the carbon conversion is calculated using Equation 9 (partial derivate of Equation 5). The overall error is calculated using the fuel gas composition shown in Figure 11 as a typical example. Table 11 summarises the measured experimental values, the associated errors and the influence each error has on the final value. The largest contribution to the over all error ($\pm 7.4\%$ abs. in this case) is associated with the fuel feeding rate. As discussed above the fuel feeding rate for each experiment can be calculated accurately. The large error is associated with the repeatability of the feeding rate. It is reasonable to remove its contribution from the overall error if the accuracy of a single experiment is to be calculated. The resulting

overall error is therefore +/- 8.8% abs., with the uncertainty in the measurement of the volumetric flow rate as the main factor.

$$\Delta X = \left| \frac{\partial X}{\partial x_{CO}} \right| \Delta x_{CO} + \left| \frac{\partial X}{\partial x_{CO_2}} \right| \Delta x_{CO_2} + \left| \frac{\partial X}{\partial x_{CH_4}} \right| \Delta x_{CH_4} + \left| \frac{\partial X}{\partial F} \right| \Delta F + \left| \frac{\partial X}{\partial FFR} \right| \Delta FFR + \left| \frac{\partial X}{\partial F_{CO_2}} \right| \Delta F_{CO_2}$$

Equation 9

Table 11: Calculation of the linear error propagation: Measured values, associated errors and calculated values.

	CO [%]	CO2 [%]	CH4 [%]	F [l/min]	FFR [g/min]	FCO ₂ [l/min]	X [%]
Value	45.1	35.3	2.2	3.6	1.8	1.584	69.9
Error (abs.)	1.28	0.98	0.06	0.12	0.18	0.04	
errX ¹ (abs.)	0.92	0.83	0.08	5	7.4	2	16.23

¹ Effect of maximum error on the percent carbon conversion (abs.)

3.5.3.4 Repeatability of Experimental Data and Conclusion

To assess the repeatability of the experimental method a set of experiments were carried out under the same conditions:

1. Temperature: 850°C
2. Pressure: atmospheric
3. Fuel feeding rate: 1.7 g/min
4. Fluidising gas: 1.72 l/min 10% O₂/CO₂
5. Fuel: German lignite

Table 12 lists the measured (normalised) fuel gas composition and the resulting carbon conversion, under steady state condition, for these 6 experiments, plus the mean values for

each measurement and the standard deviation¹⁰. It can be seen that the standard deviation is significantly smaller than the maximum error calculated before. The conclusion from this comparison is that the differences between experiments are low compared to the maximum possible error. The differences observed are mainly a result from the low repeatability of the fuel feeding rate (last column in Table 12).

Table 12: Repeatability of the experimental set up: Measurements, mean values and standard deviation.

	CO [%]	CO2 [%]	H2 [%]	CH4 [%]	X [%]	FFR [g/min]
	44.1	36.2	17.6	2.1	70.2	1.7
	44.2	37.3	16.7	1.9	71.6	1.6
	45.1	35.3	17.5	2.2	69.9	1.8
	45.3	35.4	17.3	2.0	69.3	1.8
	43.2	37.0	17.8	2.0	66.9	1.7
	47.8	32.7	17.7	1.9	72.9	1.8
Mean	44.9	35.6	17.4	2.0	70.1	1.7
STDEV	1.6	1.7	0.4	0.1	2.1	0.1

3.5.4 Reaching Steady State

As mentioned before, for each experiment the fuel gas composition is analysed during the steady state period. However the reactor is not operated under true steady state conditions. Solids were injected into the bed, but there was no draining of ash and un-reacted carbon during the course of an experiment. This means that the concentration of ash and carbon, and the bed height (gas residence time), increased with test duration. To understand why stable gas composition is reached despite this, several factors have to be considered:

- (1) Char deactivation over time: As discussed in 2.4.4.3.5, page 55, char reactivity sharply decreases with time at high temperature. As a result, immediately after being injected char can react at a reasonable rate, but becomes quite inert after a relatively short residence time.

¹⁰ Standard deviation: $STDEV = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$

- (2) Char and ash build up in the bed: Increased bed height and increased residence time, can lead to increased extent of gasification.
- (3) Inhibition of the char-CO₂ reaction by the product CO: The reaction mechanism is discussed in more detail in 2.4.4.2.3, page 50. The important implication here is that the rate of reaction decreases with increasing CO concentration.

For gasification experiments two different cases are possible: Complete carbon conversion and incomplete carbon conversion. If the carbon conversion is complete (or near complete) no char builds up in the reactor. The time from start up until steady state is reached corresponds to the time necessary to replace the atmosphere downstream of the reactor until the point where the fuel gas is sampled for the analyser. The bed height is increasing slightly due to the ash build up, but this has no significant effect in the time scale of the experiment. However, if carbon conversion is incomplete, equilibrium between the factors listed above is reached after a certain time, leading to steady fuel gas composition. The increasing carbon content of the bed (and the increasing bed height) is at some point balanced by the deactivation of the char (char content is increasing but part of the char is inert) and the decrease in reaction rate as the CO concentration is increasing. Reaching a steady fuel gas composition makes it possible to study the effect of varying the operating parameters on the steady fuel gas composition.

4 Effect of Gasification Agent and Temperature

4.1 Introduction

Fluidised bed gasifiers require oxygen to combust part of the fuel and produce the heat required for the process, a temperature moderator to keep the bed temperature well below the ash softening point¹¹ and a gasification agent to convert the remaining fuel into fuel gas. The overall process performance, e.g. carbon conversion, fuel gas heating value and energy conversion, has to be optimised by controlling the oxidizer to fuel and gasification agent to fuel ratio. There is a minimum amount of gas necessary to fluidise the bed, but despite this, and for the sake of efficiency, it is desirable to keep the amount of oxidiser and gasification agent as low as possible. A considerable amount of energy is used in the production of pure O₂ (if used), compressing the gases¹², preheating¹³ them and finally heating them to bed temperature.

As mentioned in 2.4, page 45, increasing temperature in auto-thermal gasification requires increasing extent of combustion in the process to raise the required heat. From the point of process efficiency it would be therefore desirable to operate the gasifier at lower temperatures. However the main gasification reactions, char-steam and char-CO₂ reactions, are endothermic and the rate of reaction is very slow at less than 800°C. For lignite (a reactive fuel) at temperatures below 750°C, the reactions can be considered to be at standstill [153]. Therefore in order to maximise carbon conversion the temperature has to be increased. Fluidised bed gasifiers are normally operated between 850°C and 1000°C, depending on the ash properties, as ash softening has to be avoided.

In this chapter the influence of different gasification agents and bed temperature on the process performance for O₂/CO₂ blown gasification are investigated. The first objective of the research work carried out for this chapter was to obtain data about the overall process performance and to judge the potential of an O₂/CO₂ blown process. The second objective is

¹¹ This is not the case for the KRW reactor, details are given in 2.5.3.4, page 66.

¹² All large scale process operate at elevated pressure – the effect of pressure is discussed separately in 6, page 146.

¹³ Normally to 400 - 500°C

to gain a better understanding of the mechanism involved in the fuel conversion and to see how this can be used to develop strategies to optimise the process performance.

For this study the following approach is chosen: Firstly, the gasification of fuels is divided into three processes. pyrolysis, partial combustion and gasification and secondly the influence of temperature is investigated independently from the fuel to oxidizer ratio by using the capability of the experimental set up to heat the process externally to any desired temperature. The discussion of the results is separated into two main sections. In the first section the four main parameters of the process and their influence on the overall performance are investigated: (1) pyrolysis and partial combustion, (2) fuel to oxidizer ratio (pure O_2 is used), (3) fuel to gasification agent ratio, and (4) differences between steam and CO_2 as gasification agent. The second section summarises the findings according to the influence of temperature on the process performance, the influence of gasification agent and possible strategies to optimise the process.

All experiments were carried out under atmospheric pressure with GL as fuel. The main parameters used to judge the process performance are: fuel gas composition and heating value, carbon conversion and energy conversion. To gain an insight into the underlying reactions taking place, the product distribution of combustion, the steam and CO_2 decomposition and the hydrogen product distribution (fraction of hydrogen in the fuel gas as H_2 , H_2O and CH_4) are estimated. In addition the results for the char gasification with steam and CO_2 are compared with a Langmuir Hinshelwood (LH) type of rate equation.

4.2 Pyrolysis and Partial Combustion

4.2.1 Background

It is desirable to optimise the energy conversion (amount of CO , H_2 and CH_4) during pyrolysis in order to achieve high process efficiency and to reduce the amount of oxidizer/gasification agent to convert the remaining fuel. In the case of partial combustion the production ratio of CO and CO_2 is of interest. A high yield of CO is desirable as the amount of fuel converted to CO_2 should be kept at a minimum to obtain high energy conversion and a fuel gas with high heating value. On the other hand, complete combustion to CO_2 produces more heat and a smaller fraction of fuel has to be combusted to raise the required energy.

These parameters can be estimated by carrying out separate pyrolysis experiments and partial combustion experiments. The objectives of these experiments were to see how the fuel gas composition and carbon conversion changes with pyrolysis temperature and to estimate the fraction of fuel converted by combustion to CO and CO₂.

4.2.2 Experimental Program and Fuel Gas Composition

Experiments were carried out at atmospheric pressure with GL as fuel. Fuel was pyrolysed under a nitrogen atmosphere at 750°C, 850°C and 950°C. Conditions were chosen to be comparable to the gasification experiments: $F_{in}(N_2) = 1.76$ l/min and $u_s = 0.16 - 0.18$ m/s. For the partial combustion experiments 10% of the N₂ was replaced with O₂ to achieve an O/C ratio of 0.2. The resulting fuel gas composition is summarised in Figure 15. It shows the fuel gas composition and the experimental and theoretical (Boudouard equilibrium) CO/CO₂ distribution in the fuel gas.

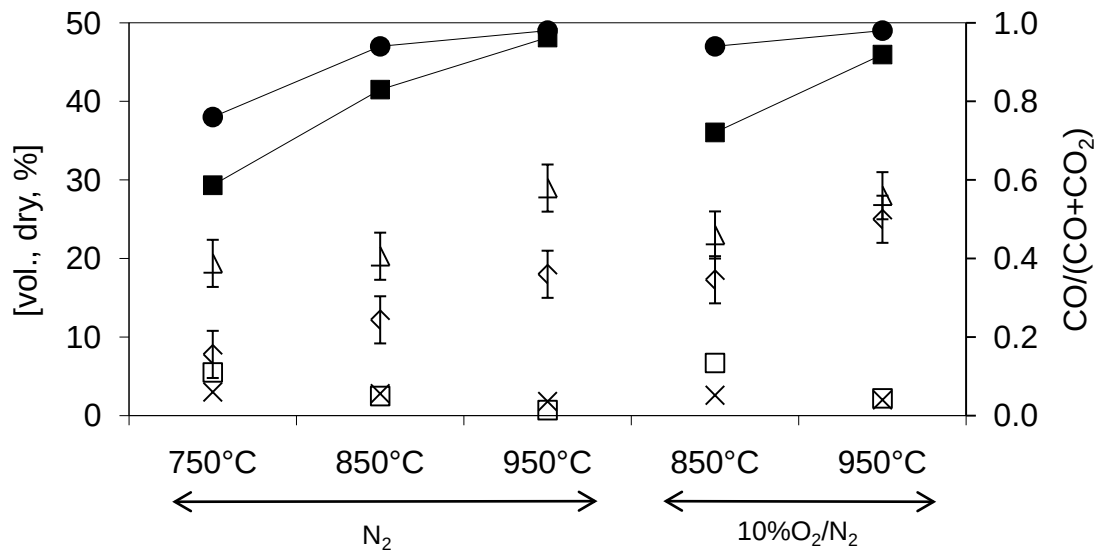


Figure 15: Pyrolysis in N₂ and partial combustion in 10% O₂/N₂ of German lignite at different temperatures. (Gas composition: □ CO₂, ◇ CO, Δ H₂, × CH₄, Balance: N₂, CO-CO₂ distribution: ■ experimental, ● calculated)

4.2.3 Discussion

Pyrolysis: Increasing pyrolysis temperature clearly increased concentration of released H₂ and CO while CH₄ and CO₂ decreased. Care has to be taken when evaluating the hydrogen values. As explained in 3.2.1.2, page 82, with N₂ present in the fuel gas, the H₂ value could only be estimated and has a large error associated with it. Therefore, only the trend, a sharp increase with temperature, is used and not the absolute values. Comparing the CO/CO₂ ratio

with the Boudouard equilibrium values at different temperatures, it can be seen that at 950°C, experimental values reach equilibrium concentration. The high concentrations of H_2 and CO at 850°C and 950°C indicate the importance of pyrolysis on the overall fuel conversion. Figure 16 shows the carbon conversion as a result of pyrolysis. With pyrolysis temperature increasing from 850°C to 950°C, carbon conversion increases from 25% to 45%. It has to be noted that carbon conversion here is calculated only based on solid carbon to CO , CO_2 and CH_4 . Fuel to tar carbon conversion is not included (the amount of tar leaving the reactor with the fuel gas under these conditions can be assumed to be very low as shown in 8.2, page 176).

Partial Combustion: Comparing the fuel gas composition from partial combustion with the fuel gas composition from pyrolysis, it can be seen that the concentration of CH_4 stays constant, H_2 decreases while CO and CO_2 increase. Part of the H_2 released during pyrolysis is combusted to water by the added O_2 . The remaining O_2 reacts with carbon to form CO_2 , which can subsequently react with fuel char to form CO . Overall, these reactions increase the carbon content of the fuel gas, but decrease the CO/CO_2 ratio slightly as can be seen by comparing it to the theoretical Boudouard equilibrium in Figure 15. Subtracting pyrolysis data from the data obtained during partial combustion, it can be calculated that at 850°C, 80% of the injected O_2 reacts to CO_2 (remaining forms CO), while at 950°C this value decreases to 30%.

Carbon Conversion: Figure 16 shows the carbon conversion at 850°C and 950°C for pyrolysis and partial combustion and the contribution of CO , CO_2 and CH_4 to the overall conversion. Carbon conversion under pyrolysis conditions is 29% at 850°C and 44% at 950°C, whilst the addition of O_2 increased the conversion to 45% and 55% respectively. The overall contribution of CH_4 is relatively small in all cases. The contribution of CO_2 to the overall conversion increased with O_2/N_2 mixtures compared to pyrolysis conditions, as additional CO_2 is formed from combustion. In summary, the carbon conversion during pyrolysis is significant and shows the importance of the pyrolysis step in the overall process.

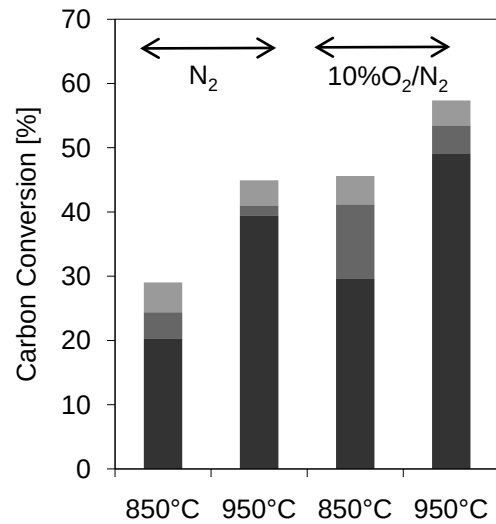


Figure 16: Carbon Conversion from pyrolysis and O_2/N_2 gasification of German lignite at different temperatures. Contribution of $\blacksquare$ CO, $\square$ CO_2 and $\blacksquare$ CH_4 to overall all carbon conversion.

4.3 Effect of O/C Ratio

4.3.1 Background

The energy for auto-thermal gasification is provided by combusting part of the fuel. For this project a resistance heater was developed, powerful enough to provide all the required heat to operate the gasifier up to 950°C. No extra heat from combustion within the reactor was necessary. Therefore it was possible to investigate the influence of the oxygen-carbon ratio independently from the gasification temperature. The relative amount of oxygen entering the reactor is given as oxygen to fuel-carbon ratio (O/C ratio, molar basis). Increasing O/C ratio could also be used to increase carbon conversion as the reaction with O_2 under this condition is always complete. In a large scale process this is however not a feasible option as it would cause a number of changes in the process balance and would require multiple changes in the process configuration. More O_2 in the system would mean more heat generated and in order to keep a constant gasification temperature this would require either increasing the fuel feeding rate or the amount of moderator (steam or CO_2). In addition, the CO_2 content of the fuel gas would increase. Therefore the O/C ratio is normally a fixed value and depends on the heating value of fuel and the overall requirements of a particular gasifier, like temperature. In large scale operation the O/C ratio is between 0.3 – 0.6 (range estimated from data given by Higman [7] and Collot [1]). In externally heated laboratory scale reactors it is not possible to operate with such high levels of oxygen as it would cause excessive temperatures in the spout region. Experimental work is carried out with an O/C ratio between 0 and 0.2. This allows investigating the effect of changing O/C ratio on operability, carbon conversion and energy conversion.

4.3.2 Experimental Program and Fuel Gas Composition

Experiments were carried out at atmospheric pressure with GL as fuel. Fuel was gasified at 750°C, 850°C and 950°C using different O_2/CO_2 mixtures (O_2 0%, 5% and 10%). Resulting O/C ratio were: 0, 0.1 and 0.2. The total flow rate entering the reactor was kept constant. F_{in} : 1.76 l/min and u_s = 0.16 - 0.18 m/s. Resulting fuel gas composition is summarised in Figure 17.

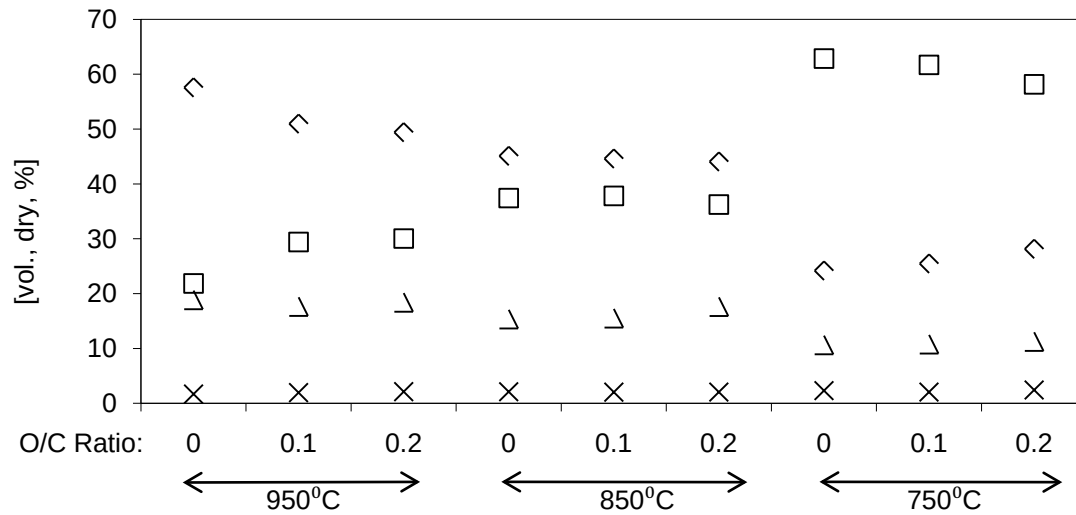


Figure 17: Oxy-fuel gasification of German lignite at different temperatures and O/C ratios – Fuel gas composition (◇ CO, □ CO₂, Δ H₂, × CH₄).

4.3.3 Discussion

4.3.3.1 Gasification Reaction and Carbon Conversion

Comparing fuel gas composition data from Figure 17 and carbon conversion from Figure 18 the following trend with increasing O/C ratio can be established:

	CO	CO ₂	Carbon Conversion
750°C	↑	↓	↑
850°C	→	→	↑
950°C	↓	↑	↓

It can be seen that for 750°C and 850°C the carbon conversion is increasing with increasing O/C ratio. At 950°C the carbon conversion decreases with increasing O/C ratio. Further investigation revealed that it is an effect of de-fluidisation in the bed. This issue is discussed separately in more detail below, while the trends at 750°C and 850°C are discussed here.

750°C: The carbon conversion increases from 34% to 44% with increasing O/C ratio while the CO₂ concentration decreases and CO concentration increases. Firstly, it is important to note that carbon conversion is not complete under this condition and therefore injected O₂ can react with char and increases the carbon conversion. Secondly, it can be estimated that approximately 60-70% of the injected O₂ reacts to form CO₂ while the rest forms CO (for estimation see previous section). This explains that the concentration of CO increases and that of CO₂ decreases in the fuel gas. More fuel carbon converted to CO, results in a fuel gas with higher heating value (increase from 5.1 MJ/m³ to 5.7 MJ/m³, Figure 20) and an overall higher energy conversion (from 31% to 36%, Figure 19).

850°C: Carbon conversion increases from 60% to 70% while concentrations of CO and CO₂ in the fuel gas stay constant. As before, conversion is not complete and additional char is consumed by the reaction with additional O₂. However the data indicated that all the injected O₂ is converted into CO₂ (CO/CO₂ ratio of the fuel gas is constant despite increase in carbon conversion). As a result, the energy conversion stays constant (66%, Figure 19), as does the heating value of the produced gas (8 MJ/m³, Figure 20).

Figure 21 shows the carbon conversion at different temperatures from pyrolysis, partial combustion and oxy-fuel gasification. For all three gaseous environments it can be seen that carbon conversion increases almost linearly with temperature. Assuming the overall conversion is the summation of the three separate processes, it can be estimated that at 850°C, 30% of the conversion results from pyrolysis, 10% from combustion and 30% from char-CO₂ gasification.

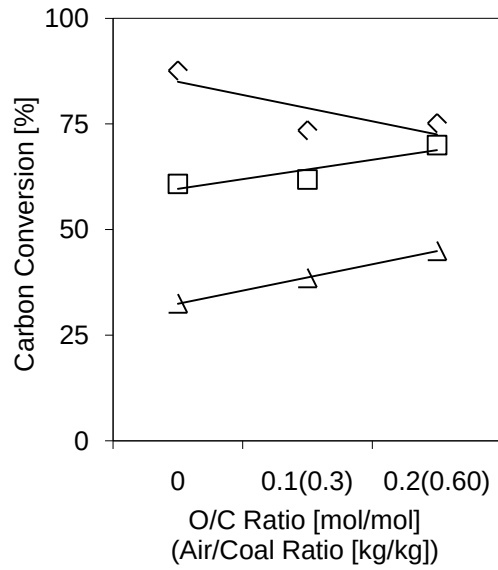


Figure 18: Oxy-fuel gasification of German lignite at different temperatures and O/C ratios – Carbon Conversion (◇ 950°C, □ 850°C, Δ 750°C).

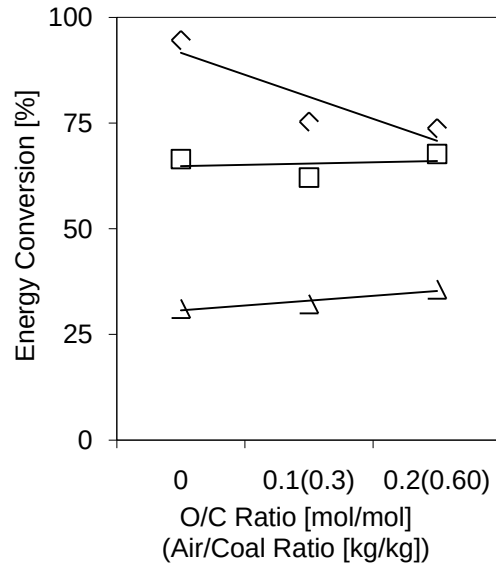


Figure 19: Oxy-fuel gasification of German lignite at different temperatures and O/C ratios – Energy Conversion (◇ 950°C, □ 850°C, Δ 750°C).

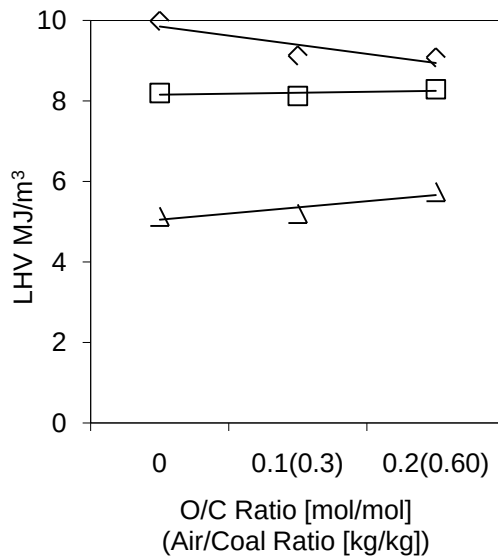


Figure 20: Oxy-fuel gasification of German lignite at different temperatures and O/C ratios – Fuel gas heating value (◇ 950°C, □ 850°C, Δ 750°C).

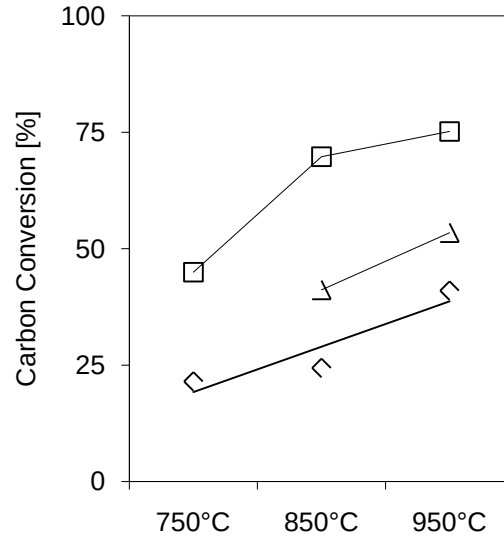


Figure 21: Carbon Conversion from pyrolysis ◇, O₂/N₂ combustion Δ and O₂/CO₂ □ gasification of German lignite at different temperatures.

4.3.3.2 Hydrogen Product Distribution

For this set of experiments, 73% of the hydrogen enters the reactor as fuel-hydrogen, while the rest is from fuel-moisture. The hydrogen product distribution is shown in Figure 22. Hydrogen to CH_4 conversion was between 6 - 7% for all conditions investigated. CH_4 is produced mainly during pyrolysis and reaches a maximum at 750°C. Its gas phase concentration is controlled by the endothermic steam methane reforming reaction. Equilibrium predicts decreasing CH_4 concentration with increasing temperature. However the activation energy of the non catalytic steam reforming reaction is very high and the actual decrease in CH_4 concentration is therefore limited. The formation of CH_4 from H_2 and CO is only relevant under elevated pressure. In addition, these results indicate that there is no direct combustion of CH_4 with increasing O/C ratio, after it is formed by pyrolysis.

The concentration of H_2 increases with temperature (11 - 12% at 750°C to 18 - 19% at 950°C) but there seems to be no significant change with O/C ratio. To assess why levels of hydrogen increase with increasing temperature, three factors have to be taken into account: (1) hydrogen release during pyrolysis, (2) char-steam reaction, and (3) the thermodynamic equilibrium. Pyrolysis experiments show a sharp increase of H_2 in the pyrolysis gas with increasing temperature. The extent of the endothermic char-steam reaction increases with temperature. Thermodynamic equilibrium calculations carried out for these conditions predict no significant change of H_2 release with increasing temperature (Chapter 9, page 203). However, the carbon conversion increases at the higher temperatures (for experiment with 100% CO_2) and this increases the amount of carbon in the gas phase as CO . This moves the WGS equilibrium towards higher percentage of H_2 . Summarising the available information, an increase of hydrogen release during pyrolysis and an increase in extent of char-steam reaction seem to have the strongest effect on the final hydrogen content of the fuel gas. As in the case of CH_4 , no effect of increasing O/C ratio on the H_2 concentration is noted.

Steam in the fuel gas is made up of unconverted fuel-moisture, steam release during pyrolysis and as a product of the reverse water-gas shift reaction. As for H_2 , the main reasons for changes in concentrations are the influence of temperature on the steam-char reaction and the release of steam during pyrolysis.

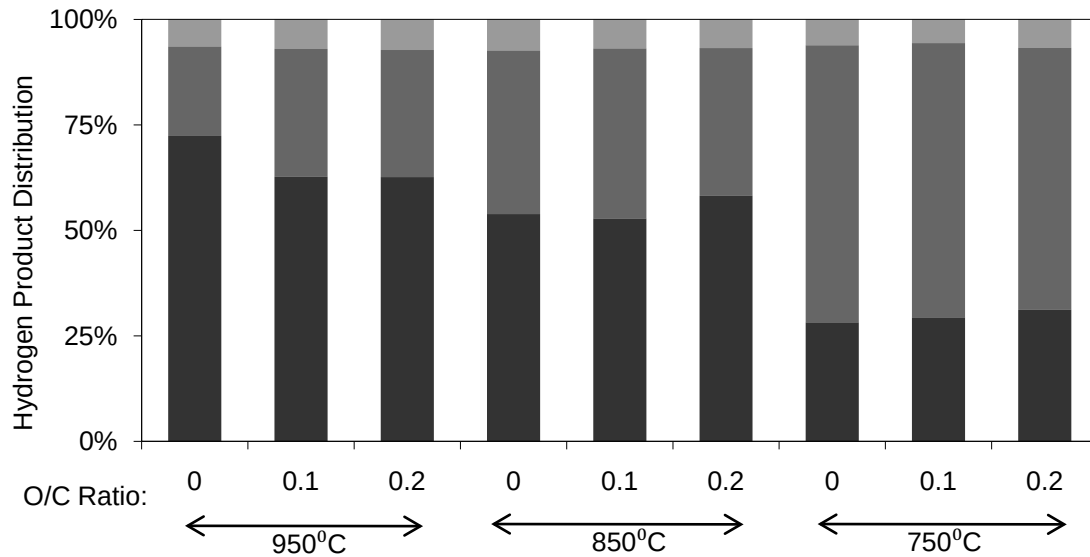


Figure 22: Oxy-fuel gasification of German lignite at different temperatures and O/C ratios – Hydrogen Product Distribution (■ H₂, ■ H₂O, ■ CH₄).

4.3.3.3 Agglomeration of Bed Material at 950°C

The decrease in the carbon conversion at 950°C with increasing O/C ratio was the first indication of a decrease in mixing efficiency in the bed. Subsequent analysis of the bed material recovered after the experiments revealed that at 950°C with 0.1 and 0.2 O/C ratio large agglomerates had formed in the bed.

To confirm that the agglomerates formed during gasification and not during the time the bed was cooling down, two different approaches were chosen: (1) Three separate thermocouples were installed at different bed heights to monitor the temperature distribution in the bed. (2) The experiment was interrupted at different times (after 15, 25 and 35 min) to see if the extent of agglomeration was increasing over time. The findings of both tests are summarised in Figure 23. The temperature profile over time shows that the temperatures measured at the 3 different heights of the bed were almost the same during start up and the first 8 min after fuel feeding was switched on. After that a rapid decrease of the bed temperature at the bottom of the reactor was recorded. Initially it was attempted to compensate this with increasing the heat input from the external heater, but it had no effect on the bottom temperature. Pictures of the agglomerated material recovered after different experimental times (Figure 24) show that

the agglomerates built up in the cone of the bed around the injection spout. Over time the agglomerated material first grew upwards along the spout and then grew in width. Defluidisation of the bottom part of the bed and related decrease in heat transfer from the walls explains the decrease in temperature detected by the bottom thermocouple. Probably due to the high spout velocity (approximately 4 times bed velocity) the agglomerating material didn't block the injection of solid material. The spout maintains a channel through the bed material.

Agglomeration of silica bed material in fluidised bed reactors is a well known phenomenon. Na and K from the lignite ash together with Si from the sand can form low melting silicates which act like a glue between the sand particles [141, 154]. The build up of agglomeration seems to be directly related to the availability of free oxygen. No agglomeration was detected for experiments with pure CO₂ and agglomerated particles built up around the spout where levels of oxygen were at their highest. The particle temperature in the spout region where oxygen reacts with char and volatiles is probably significantly higher than the overall bed temperature and the main reason for the agglomeration. Avoiding agglomeration by using different types of bed material is discussed in 5.4, page 147. The influence of fuel composition on the agglomeration is discussed in 7.2, page 166.

Figure 24 shows pictures of the different types of bed material recovered. The agglomerated material (cone sitting in the bottom of the bed) consists of the silica sand (white particles) and ash (orange particles). Char (black particles) can only be found on the outside of the agglomerated material which indicates that all char inside is consumed over time by the oxygen (only the char in the agglomerated material near the spout is consumed completely, this is not related to the overall carbon conversion). The particles on the outside of the cone are from contamination during the recovery process. Loss of fluidisation affects the mixing of the injected coal particles with hot bed material and affects gasification performance. In particular, agglomeration of static material in the cone of the bed prevents material flowing downwards and its subsequent entrainment in the spout gas. Therefore the advantage of the spouted bed design in increasing mixing is lost. Interestingly the increasing amount of agglomerates in the bed does not have an effect on the stability of the gasification process. After the start up period, a stable steady state mode of operation is reached. Only the comparison of the steady state fuel gas compositions and carbon conversion shows the effect of increasing agglomeration.

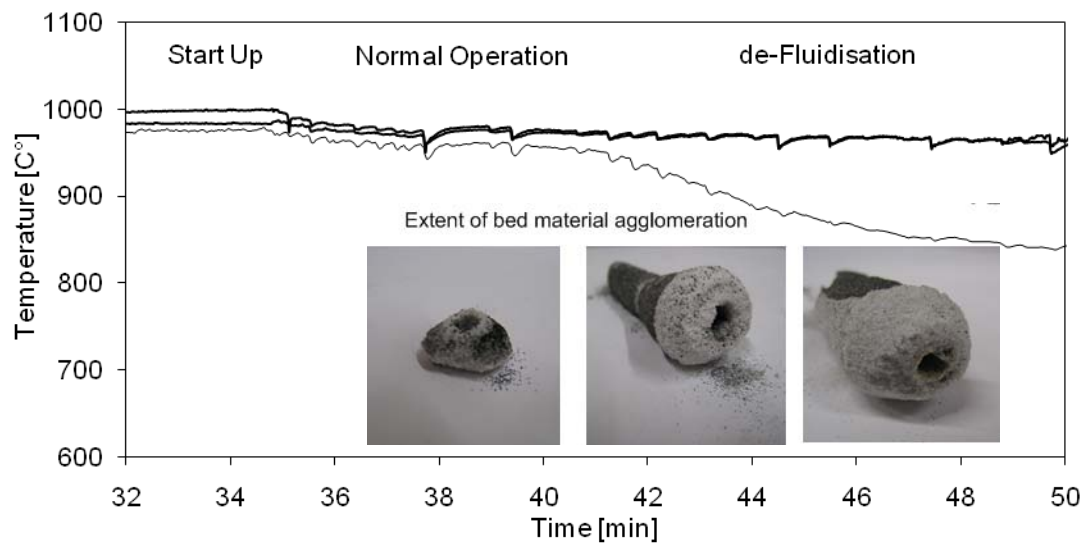


Figure 23: Partial de-fluidization and agglomeration of bed material.

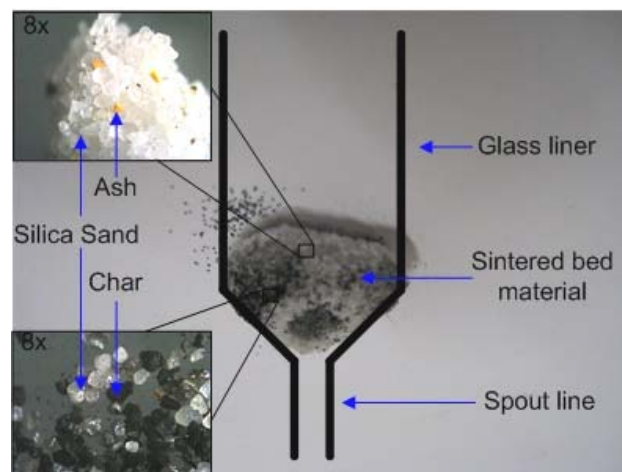


Figure 24: Agglomerated bed material from the bottom the reactor. Particles: Char (black), sand (white), ash (orange)

4.4 Effect of CO₂/C Ratio

4.4.1 Background

The CO₂/C ratio is comparable to the steam/coal ratio for air blown gasification. Increasing the CO₂/C ratio increases the amount of reactive gas per unit fuel and therefore affects the char gasification. However, increasing the amount of CO₂ entering the reactor increases the heat required to heat the input stream to gasification temperature. For an efficient gasification process the amount of CO₂ and O₂ used has to be optimised to achieve maximum carbon and energy conversion on the one hand, while keeping the amount of CO₂ and O₂ at a minimum¹⁴.

4.4.2 Experimental Program and Fuel Gas Composition

Experiments were carried out at atmospheric pressure with GL as fuel. Fuel was gasified at 750°C, 850°C and 950°C using different CO₂/C ratios. The resulting fuel gas composition is summarised in Figure 25. All experiments were carried out with 100% CO₂ as fluidising gas. Different CO₂/C ratios were achieved by changing the amount of CO₂ injected into the reactor and keeping the fuel feeding rate constant. This changes the superficial velocity but on the other hand keeps the contribution of pyrolysis to the overall performance constant. The change in superficial velocity is not seen as significant under these conditions as discussed in detail in 3.5.2, page 98.

¹⁴ As mentioned before, each gasification process has specific constraints regarding the amount of oxidant, moderator, gasification agent and fluidising agent. Therefore any optimisation for a commercial process would have to be carried out in the context of these requirements.

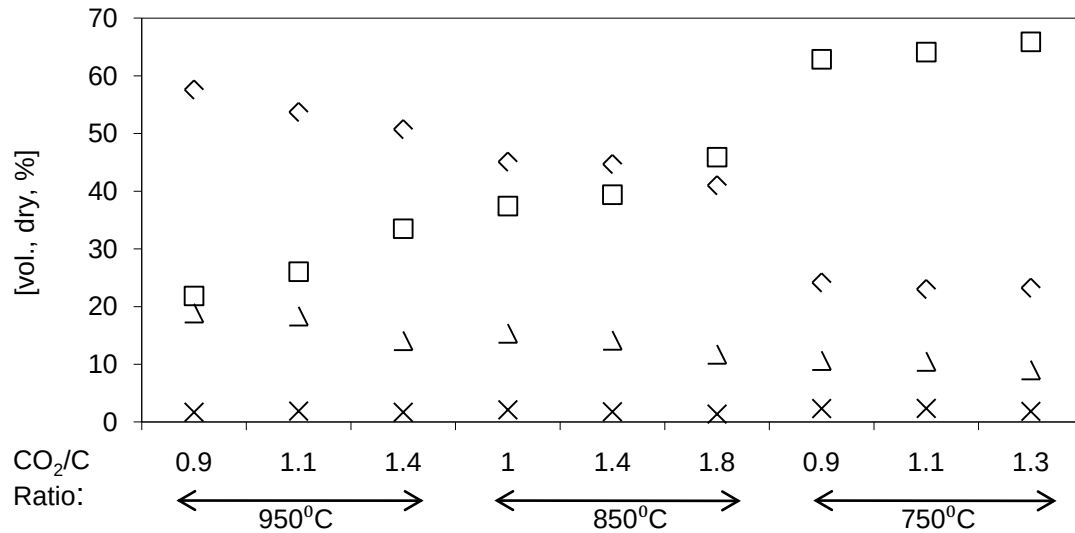


Figure 25: Oxy-fuel gasification of German lignite at different temperatures and CO₂/C ratios. (□ CO₂, ◇ CO, Δ H₂, × CH₄)

4.4.3 Discussion

4.4.3.1 Gasification Reaction and Carbon Conversion

Combining the information about the fuel gas composition from Figure 25 and the resulting carbon conversion (Figure 26), the following trends can be established for increasing CO₂/C ratio: (1) decrease in CO (increase in CO₂) concentration and constant (average 85%) carbon conversion at 950°C, (2) slight increase in CO (decrease in CO₂) for 850°C but clear increase of carbon conversion from 60% to 85% and, (3) Increase in CO₂, decrease of CO, and increase of carbon conversion from 32% to 37% at 750°C.

Maximum possible carbon conversion: It seems that at 950°C, a maximum possible carbon conversion is reached. These experiments were carried out with a high superficial velocity (up to $u_s = 0.27$ m/s). Recovering the bed material after the tests showed that this results in a larger amount of char particle being ejected from the bed and collected in the tar trap. Therefore the limit of 85% conversion is probably due to the carbon loss during the experiment. At 950°C an increase in CO₂/C ratio does not increase carbon conversion. The char-CO₂ reaction at this temperature seems to be fast and not affected by the increasing amount of CO₂ anymore. Increasing the CO₂/C ratio diluted the fuel gas and therefore decreased the heating value from 10 to 8.5 MJ/m³ (Figure 27).

Increase of carbon conversion: At the lower temperatures, 750°C and 850°C, increasing CO₂/C ratio increased the carbon conversion from 32% to 37% at 750°C and from 60% to 85% at 850°C. At 750°C the char-CO₂ reaction is very slow. The majority of the carbon conversion is a result of pyrolysis. Therefore increasing CO₂/C ratio has only limited effect on overall conversion. The result at 850°C is different from that: The char-CO₂ reaction seems to be fast enough to be influenced by the partial pressure of CO₂. At a CO₂/C ratio of 1.4 it reaches the maximum carbon conversion of 85% as already discussed. At both temperatures, excess CO₂ dilutes the fuel gas and decreases its heating value by a similar amount (Figure 27).

CO₂ conversion: CO₂ conversion is an indicator for the fraction of CO₂ used as gasification agent compared to the CO₂ passing the reactor as quasi inert gas. Maximising the CO₂ conversion is vital for the process efficiency as the amount of unconverted CO₂ increases the amount of energy required to heat up the input gas stream to gasification temperature¹⁵. The CO₂ conversion can be estimated from the CO₂ balance for the reactor for each condition. It has to be noted that the calculated values are an overall balance. They include the effect of pyrolysis and water-gas shift reaction. However, the influence of pyrolysis is considered to be small in comparison with the total amount of CO₂ in the fuel gas and there seems to be no significant effect from the water-gas shift reaction on the concentration of CO and CO₂ (discussed below). Therefore the overall balance of CO₂ in the process is seen as a reasonable approach to calculate the CO₂ conversion. Figure 28 shows the results: At 950°C the carbon conversion had already reached a maximum and no extra CO₂ is converted (the fraction of CO₂ conversion decreases). A different situation can be observed at 750°C, where CO₂ conversion slightly increases as an effect of increasing carbon conversion. The most interesting case is 850°C. Under the conditions used, a maximum in CO₂ conversion can be observed at a CO₂/C rate of 1.4. At this point, carbon conversion versus CO₂ conversion reaches a maximum.

¹⁵ It has to be mentioned that the amount of CO₂ in a fluidised bed gasifier cannot be varied independently as a certain amount is required to ensure good fluidization of the bed.

Reaction mechanism: The reaction of CO₂ with solid carbon can be described by a Langmuir-Hinshelwood type of rate equation (see 2.4.4.2.350). In this work the equation derived by Ergun [57] is used. By qualitative analysis [155] of the rate equation the following trends can be established and subsequently compared with experimental results:

- (1) Rate of reaction increases with increasing partial pressure of CO₂

$$r_s \sim p(\text{CO}_2) \quad \text{Equation 10}$$

This is clearly confirmed by the results. From Figure 26 it can be seen that for 750°C and 850°C the carbon conversion is virtually directly proportional to the CO₂/C ratio. This effect is increasing with temperature. However at 950°C carbon conversion is already complete at the lowest CO₂/C ratio investigated and therefore no effect can be noted anymore.

- (2) At very high partial pressure of CO₂ the rate of reaction becomes independent of the CO₂ partial pressure¹⁶.

$$r_s \sim \frac{p(\text{CO}_2)}{1+p(\text{CO}_2)} \quad \text{Equation 11}$$

From the experimental results this is hard to judge as at high CO₂/C ratio, carbon conversion is complete at higher temperatures. Looking at the results obtained at 750°C it would be reasonable to assume that the carbon conversion will not continue to increase until it reaches completion with increasing CO₂/C ratio. There will be an upper limit to it according to Equation 11.

- (3) The reaction is inhibited by its product CO.

$$r_s \sim \frac{1}{p(\text{CO})} \quad \text{Equation 12}$$

Increasing CO₂/C ratio reduces the partial pressure of CO in the gas by dilution with excess CO₂ as discussed above. This would reduce the inhibiting effect and increase rate of reaction. However from the results obtained it is not possible to separate the

¹⁶ For runs at atmospheric pressure with 100% the partial pressure of CO₂ in the gasification agent is 1 bar. However the char gasification takes place in a gas mixture of the gasification agent and product gases from pyrolysis and gasification. Therefore increasing the CO₂/C ratio is increasing the partial pressure of CO₂ in this environment.

effect of increasing partial pressure of CO_2 and decreasing partial pressure of CO from each other.

Overall the underlying reaction mechanism as predicted by a LH rate equation could be confirmed by the results. However, the experimental set up used in this study is not suitable to obtain a quantitative analysis of the char- CO_2 reaction, e.g. activation energy and frequency factor, as effects due to pyrolysis, gas phase reaction and reactor configuration cannot be separated from the char- CO_2 reaction. An additional problem is the different reactivity of the char in the reactor as a result of the residence time distribution. However from results obtained in 6.6, page 164 it can be concluded that char injected in the reactor is deactivated very quickly (less than 10 s) and therefore it could be assumed that only fresh char is reacting.

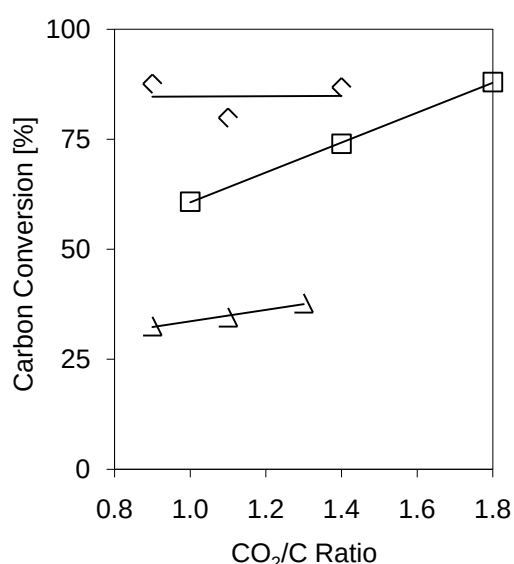


Figure 26: Oxy-fuel gasification of German lignite at different temperatures and CO_2/C ratios – Carbon Conversion (◇ 950°C, □ 850°C, Δ 750°C).

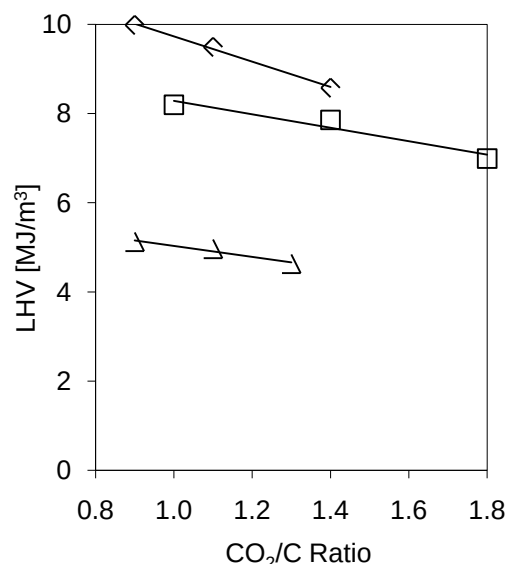


Figure 27: Oxy-fuel gasification of German lignite at different temperatures and CO_2/C ratios – Fuel gas heating value LHV (◇ 950°C, □ 850°C, Δ 750°C).

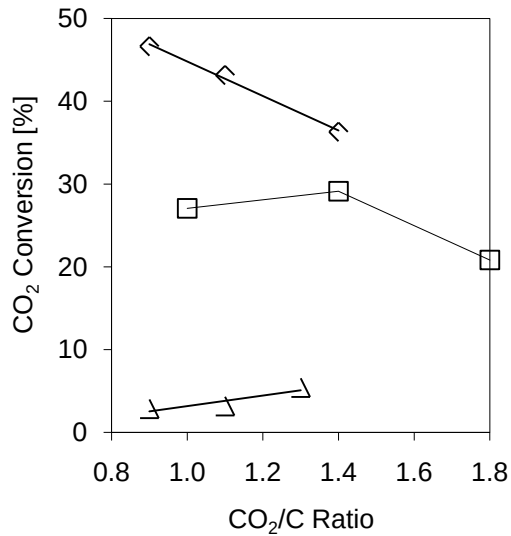


Figure 28: Oxy-fuel gasification of German lignite at different temperatures and CO₂/C ratios – CO₂ conversion (◇ 950°C, □ 850°C, Δ 750°C).

4.4.3.2 Hydrogen Conversion and Product Distribution

The hydrogen product distribution is shown in Figure 29. Compared to the results discussed in 4.4.3.2 the trends look very similar. The amount of CH₄ is similar (6% - 8%) for all conditions investigated while no significant trend in amount of H₂ with increasing CO₂/C ratio can be seen. It could be argued that increasing levels of CO₂ increase the extent of char-CO₂ reaction and at the same time decrease the extent of char-steam reaction. However, considering the relatively low operating temperatures and the fact that char-steam reaction is faster than char-CO₂ reaction this is unlikely in this case. In summary, gasification temperatures and with it the extent of char-steam reaction plus CH₄/H₂/water release during pyrolysis at different temperatures are the dominating factors in establishing the hydrogen product distribution.

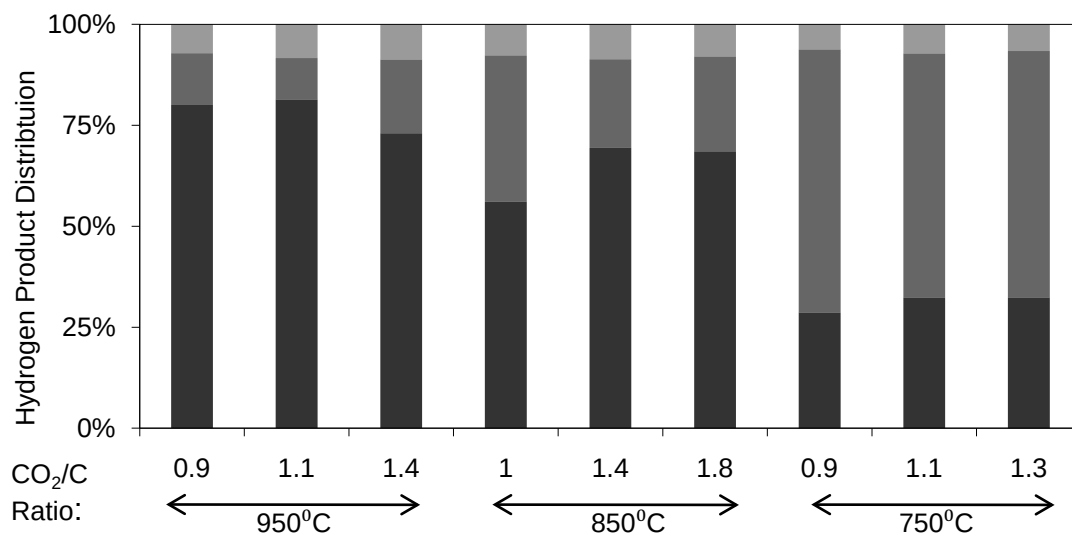


Figure 29: Oxy-fuel gasification of German lignite at different temperatures and O/C ratios – Hydrogen Product Distribution (■ H_2 , ■ H_2O , ■ CH_4).

4.5 Effect of Steam/CO₂ Ratio

4.5.1 Background

It is well known that the gasification with H₂O is faster at lower temperatures compared to the gasification reaction with CO₂. To investigate the significance of this in the current set up, CO₂ was stepwise replaced with steam as gasification agent. Adding steam to a primary O₂/CO₂ blown process could be considered for two reasons: using the faster char-steam rate to increase carbon conversion and heating value of the fuel gas and increasing the H₂/CO ratio in the product gas if required by downstream applications.

4.5.2 Experimental Program and Fuel Gas Composition

Experiments were carried out at atmospheric pressure with GL. Fuel was gasified at 750°C, 850°C and 950°C using different CO₂/steam ratios (0, 0.3, 1 and 2.3). This results in 0, 25%, 50% and 75% of CO₂ being replaced by steam (molar basis). No O₂ was added in this set of experiments. The total flow rate entering the reactor was kept constant: $F_{in} = 2.64$ l/min and $U_s = 0.24 - 0.27$ m/s. The resulting fuel gas compositions are summarised in Figure 30.

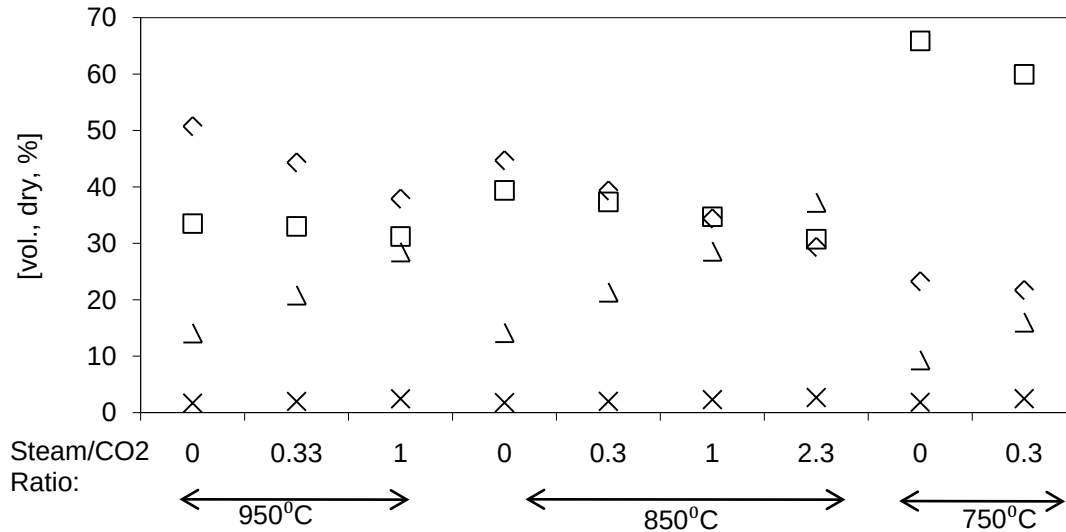


Figure 30: Oxy-fuel gasification of German lignite at different temperatures and Steam/CO₂ ratios. ($\diamond$ CO, $\square$ CO₂, Δ H₂, $\times$ CH₄)

4.5.3 Discussion

4.5.3.1 Gasification Reaction and Carbon Conversion

With increasing steam/CO₂ ratio, the char-CO₂ reaction is partially replaced with char-steam reaction. This change can be clearly identified in the fuel gas composition in Figure 30. Replacing CO₂ with steam increases the H₂ concentration and decreases the CO concentration in the fuel gas.

Carbon Conversion: The conditions for the initial experiments (steam/CO₂ = 0) were chosen in a way that the carbon conversion at 750°C and 850°C were incomplete while at 950°C carbon conversion was complete (discussed in 4.4, page 121). Figure 31 shows the change in carbon conversion with increasing steam/CO₂ ratio. It can be seen that replacing 25% of CO₂ by steam increased the carbon conversion at 750°C and 850°C while at 950°C no change occurred. This result is similar to the one discussed in 4.4: at 950°C, maximum possible carbon conversion is achieved, independent of CO₂/C ratio and steam/CO₂ ratio. At 850°C carbon conversion is increased by 25% steam to a level comparable with results from experiments carried out at 950°C. Further increasing steam/CO₂ ratio did not change the carbon conversion at 850°C. As for 950°C, it is assumed that the maximum possible carbon conversion is reached.

Steam conversion: In a similar manner as discussed in 4.4 for the CO₂ decomposition, the steam decomposition can be calculated (Figure 32). Steam input was defined as steam in the fluidising gas plus moisture in the fuel. In the case of 750°C and steam/CO₂ ratio, a negative value is calculated which indicates that more steam is generated during pyrolysis than is used in the char-steam reaction. Comparing the extent of the steam/CO₂ conversion in the char-CO₂ and char-steam reaction two observations can be made: Firstly, steam conversion is higher than CO₂ decomposition at 750°C and 850°C and secondly the extent of H₂O conversion is constant at 850°C and 950°C. These findings lead to the following conclusions: (1) At lower temperature, 750°C and 850°C, the char-steam reaction is faster than the char-CO₂ reaction (2) At 950°C no difference in the rate of reaction between char-steam and char-CO₂ can be observed (3) Steam replaces CO₂ as gasification agent proportional to its concentration in the fluidising gas as the amount of H₂ produced is increasing proportionally with the amount of steam injected (4) The char-steam reaction is not inhibited by its product H₂ in the region investigated.

Reaction mechanism: As for the char-CO₂ reaction, the reaction of H₂O with solid carbon can be described by a Langmuir-Hinshelwood type of rate equation (see 2.4.4.2, page 49). The principals of the proposed rate equations are the same as for the char-CO₂ reaction. Only the inhibiting effect by hydrogen is described differently according to the different underlying reaction mechanism. By qualitative analysis [155] of the rate equation the following trends can be established:

- (1) Rate of reaction increases with increasing partial pressure of H₂O

$$r_s \sim p(H_2O) \quad \text{Equation 13}$$

Indication of this can be seen at 850°C in the case of replacing 25% of the CO₂ by H₂O: partial pressure of steam increases together with H₂O conversion (Figure 32). The same can be seen for 750°C where the rate of H₂O conversion increases with partial pressure of steam.

- (2) At very high partial pressure of H₂O the rate of reaction becomes independent of it

$$r_s \sim \frac{p(H_2O)}{1+p(H_2O)} \quad \text{Equation 14}$$

Similar to the char-CO₂ reaction, from the experimental results this is hard to judge, as at high steam/CO₂ ratio carbon conversion is complete.

- (3) The reaction is inhibited by its product H₂

$$r_s \sim \frac{1}{f(p(H_2))} \quad \text{Equation 15}$$

As analysed and discussed before, H₂O conversion is constant and does not decrease with increasing H₂ content of the fuel gas. Therefore, there is either no inhibition of the char-steam reaction by hydrogen or it follows a rate law where the inhibition only becomes significant with very high concentrations of H₂ in the gas like the one proposed by Weeda et al. [156], Giberson and Walker [157] and Yang and Yang [158]. In this model the hydrogen inhibition is caused by dissociative chemisorption of hydrogen and the corresponding rate is:

$$r_s \sim \frac{1}{p(H_2)^{0.5}} \quad \text{Equation 16}$$

In conclusion the LH type of rate equation can qualitatively be confirmed by the experimental results.

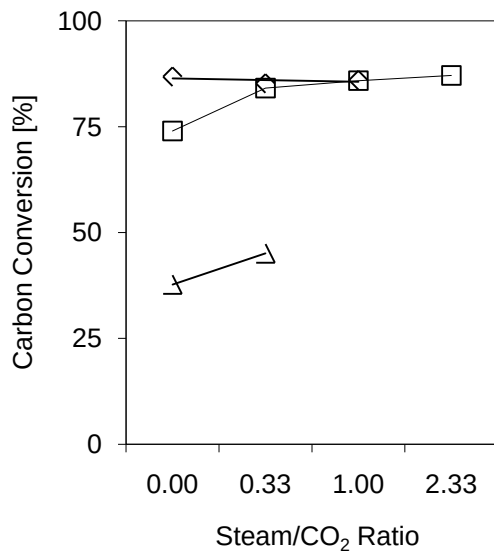


Figure 31: Oxy-fuel gasification of German lignite at different temperatures and steam/CO₂ ratios – Carbon Conversion (◇ 950°C, □ 850°C, Δ 750°C).

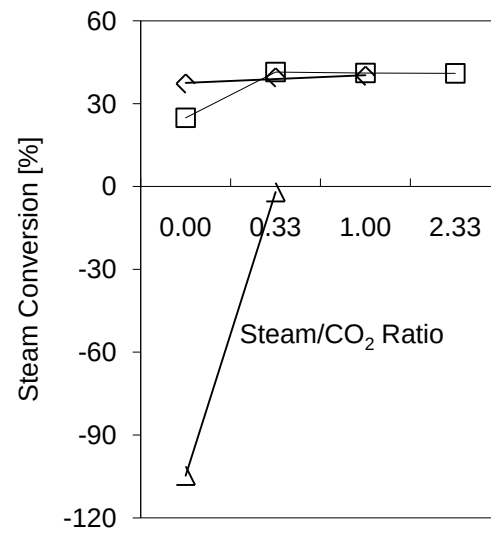


Figure 32: Oxy-fuel gasification of German lignite at different temperatures and steam/CO₂ ratios – Steam Conversion (◇ 950°C, □ 850°C, Δ 750°C).

4.5.3.2 Hydrogen Conversion and Product Distribution

Figure 33 shows the hydrogen product distribution at different temperatures and with different steam/CO₂ ratios. As mentioned before, CH₄ is mainly a product of pyrolysis and its release is fairly constant in the range tested. Therefore, total hydrogen to CH₄ conversion decreases as total hydrogen increases with increasing steam/CO₂ ratio.

The fraction of hydrogen as H₂ in the fuel gas decreases with decreasing temperature as discussed in the previous sections and with increasing steam/CO₂ ratio for 850°C and 950°C. However, as identified in Figure 32, steam conversion under these conditions is constant – 40% of the steam injected is converted into H₂ – independent of the amount of steam injected. There are two possible reasons for that: (1) the actual steam conversion slightly decreases with increasing steam/CO₂ ratios but this effect can be only seen if the fuel moisture is accounted for. (2) The extent of the fuel-moisture fuel-carbon reaction decreases as more steam is injected. At 750°C there is a slight increase of fuel hydrogen to H₂ conversion with increasing steam concentration. This agrees with the increased steam conversion in Figure 32.

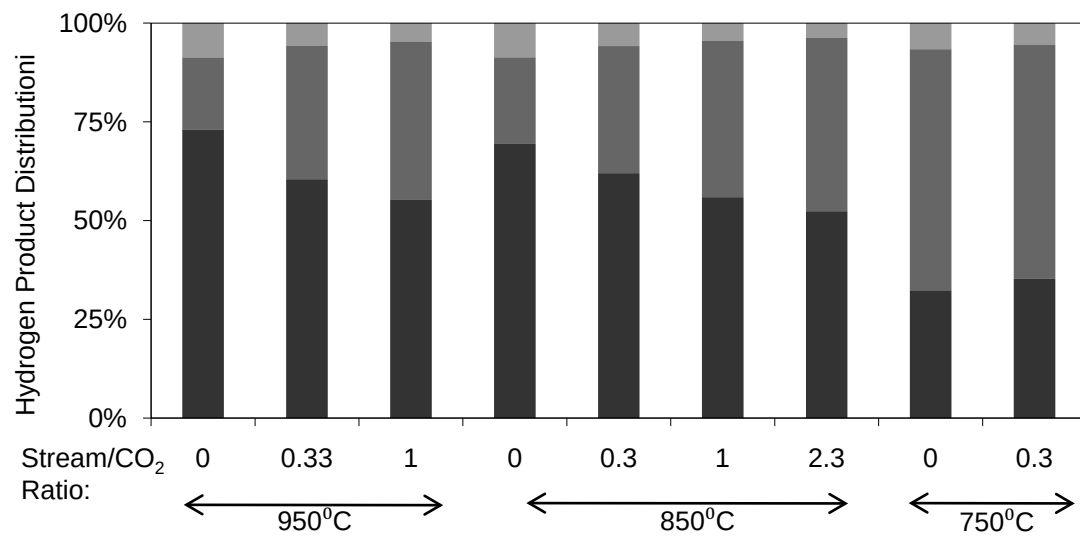


Figure 33: Oxy-fuel gasification of German lignite at different temperatures and Steam/CO₂ ratio – Hydrogen Product Distribution (■ H₂, ■ H₂O, ■ CH₄).

4.6 Summary

4.6.1 Effect of Temperature

This section discusses the effect of gasification temperature on the gasification performance. To avoid presenting the same findings twice, the results from the previous sections are summarised here focusing on the influence of temperature.

Carbon conversion: Increasing temperature increases carbon and energy conversion. The results show that gasification temperature can be decreased from 950°C to 850°C, while keeping the carbon conversion constant if: (1) the CO_2/C ratio is increased to 1.8 (2) the steam/ CO_2 ratio is increased to 0.33. In the first case this comes at the cost of having a large amount of additional CO_2 in the process, costing additional energy to heat it up and diluting the fuel gas. In the second case extra steam is needed for the process and the H_2/CO ratio of the fuel gas increases.

Methane: Independent of the gasification temperature about 6 to 7% of the total fuel-hydrogen (moisture and fuel-hydrogen) is converted to CH_4 . The main source of CH_4 is its release as pyrolysis product. CH_4 does not seem to be influenced by the equilibrium of the gas phase reaction.

Hydrogen: The amount of hydrogen in the fuel gas increased for all conditions tested. Three reasons were identified: (1) increase in hydrogen release during pyrolysis with increasing temperature (2) increasing extent of char-steam (steam from fuel-moisture) reaction with increasing temperature (3) increasing carbon conversion increases the amount of carbon in the gas phase as CO and this shifts the WGS equilibrium towards hydrogen.

Steam: The amount of steam in the fuel gas follows the inverse trend of hydrogen as both are connected by the char-steam reaction and the WGS equilibrium.

Operability: A major impact of temperature on the operability of the gasifier was noted at 950°C with oxygen in the system. The temperature in the spout caused bed material to agglomerate, affecting the gasification performance.

4.6.2 Effect of Gasification Agent

Nitrogen: Nitrogen is not a gasification agent. It was used in the pyrolysis and partial combustion experiments as fluidising agent. In larger applications, it is present if air is used as oxidiser and can be used as fluidising agent and to a certain extent as temperature moderator¹⁷.

Oxygen: With oxygen in the gasification agent part of the fuel is combusted and extra heat is produced. As discussed above, at 950°C, this extra heat was the main reason causing agglomeration and de-fluidising of the bed. At lower temperatures, increasing the amount of oxygen increased the carbon conversion. Whether the energy conversion increased as well depends on the product distribution of the carbon combustion. For the partial combustion/CO₂ gasification experiments more CO was produced with increasing temperature and therefore energy conversion was increased. In the case of O₂/CO₂ blown gasification experiments this was only the case for 750°C where about 30% of the O₂ reacted to CO. At 850°C all the O₂ was converted to CO₂ and the energy conversion did not increase with carbon conversion.

Carbon dioxide: In an O₂/CO₂ blown gasification process CO₂ is the main gasification agent. The char-CO₂ reaction is strongly temperature dependent and its rate increases with temperature. At 750°C almost no CO₂ gasification occurred, while at 950°C the rate was fast enough to achieve complete carbon conversion with a gasification agent consisting of 100% CO₂ under any conditions tested. The reaction is strongly dependent on the partial pressure of CO₂ as the rate increases with increasing CO₂/C ratio. However the extent of CO₂ conversion decreased, probably indicating inhibition by the reaction product CO. An optimum rate of CO₂ conversion was identified at 850°C and 1.4 CO₂/C ratio. In general excess CO₂ dilutes the fuel gas and more energy is required to heat up the increased volume of fluidising gas. However, in a large scale application a certain amount of CO₂ is required as fluidising agent and temperature moderator.

Steam: Up to 75% of CO₂ was replaced with steam to study the difference of the char-steam and char-CO₂ reactions. It was found that at 950°C both reactions were fast enough to

¹⁷ Energy is required to heat gases to the bed temperature.

achieve maximum carbon conversion. The rate of steam conversion was constant, indicating that in this range the reaction is not inhibited by its product H_2 . The addition of steam to a O_2/CO_2 blown fluidised bed gasification process could be useful in two ways: (1) increase H_2/CO_2 ratio in fuel gas if required (2) achieve higher carbon conversion at lower temperatures.

5 Effect of Bed Material

5.1 Introduction

Fluidised bed gasification processes use different bed materials, based on the characteristics of the process. In order to get an idea which type of bed material can be used for a process two main criteria have to be considered: The first criterion is the overall carbon conversion and ash content of the fuel. A process with relatively low carbon conversion and/or very high ash content in the fuel does not necessarily require additional bed material. The mass of accumulated carbon and/or ash is sufficient to be used as bed material. However for a process with complete or near complete carbon conversion and if a fuel low in ash is used, as it is the case for processes using lignite or biomass, additional bed material has to be used. For example sand, dolomite or olivine. The second criterion to decide if additional bed material is required is related to the desired functionality of the material. There are two main possibilities: sulphur retention and catalytic activity. For a process using fuel with high sulphur content it is certainly desirable to retain a maximum amount of sulphur in the bed. In this case, limestone or dolomite is continuously fed to the bed. The catalytic activity of certain bed material can be used to improve the process performance either by enhancing the extent of tar cracking for a process with biomass fuels or by catalytic promotion of the gasification reactions (this effect is discussed in more detail in 2.4.5, page 57).

Before the results in this chapter are discussed, it is necessary to compare the fate of solids in a large scale fluidised bed gasifier and in the lab scale gasifier used in this study. During operation solid material is fed into the bed. A certain fraction of the solids (ash, inorganic additives, carbon) are not converted to gas and build up in the bed. To obtain a stable process solid material has to be constantly removed at the bottom of the bed. Overtime the feeding, converting and removing of solids results in a steady state bed composition and bed height. However, solid removal is not possible in this laboratory scale reactor and therefore the bed composition and the bed height are changing over the duration of an experiment. Despite changing bed composition and height, stable fuel gas composition is obtained after around 10 min fuel feeding. At this point the bed contains the initial bed material, unconverted char accumulated from the start of feeding and the ash of the fuel injected so far. During steady state operation additional unconverted char and ash build up and the bed height increases. This limits the maximum duration of an experiment to approximately 60 min.

Based on the differences between the experimental set up and a large scale gasifier, the following approach was chosen in this study: the initial bed material was varied in three different ways: (1) total amount of bed material used to obtain different bed heights during steady state (2) initial amount of char and sand in the bed to change the char/sand ratio during steady state (3) different amount of sand and dolomite to change the ratio of catalytic/non-catalytic material during steady state operation.

The chapter is divided into 2 sections. In the first section different bed height and char/sand ratios are used and the influence on gasification performance is investigated while the second section investigates the influence of catalytic material on the gasification performance.

The objectives of the study are to investigate three main questions:

- (1) What is the influence of the bed height on the gasification performance? And does the increasing bed height (increasing gas residence time) increase the carbon conversion?
- (2) How does the char content of the bed influence the gasification performance?
- (3) What are the differences of silica sand and dolomite as bed material?

All experiments were carried out under atmospheric pressure with GL as fuel. The main parameters used to judge the process performance are fuel gas composition and carbon conversion. To gain an insight into the underlying reactions taking place, the CO₂ conversion and the hydrogen product distribution (fraction of hydrogen in the fuel gas as H₂, H₂O and CH₄) are estimated.

5.2 Bed Height and Carbon Content

5.2.1 Background

The effect of changing the bed height, and therefore the gas residence time and changing the char/sand ratio of the bed on the process performance has been investigated.

Before the results are discussed it is useful to establish what trends are expected based on the information available. As discussed in (3.5, page 98) 60 g of silica sand in the bed led to the best solid back mixing, as determined in the cold tests. Decreasing the amount of sand should reduce the mixing of injected solids with the preheated bed material and therefore decrease the carbon conversion. Slow mixing reduces the heating rate of the injected particles and therefore negatively affects the char reactivity. In addition, gas residence time will decrease and this should further decrease the carbon conversion. Increasing the amount of char in the bed should increase the amount of carbon in the fuel gas as more char is available to react with the fluidising gas. This would increase the overall carbon conversion. However, it has to be kept in mind that char reactivity sharply decreases with time exposed to high temperature (2.4.4.3.5, page 55). Therefore the char reservoir in the bed will be less reactive than the nascent char from the freshly injected fuel.

5.2.2 Experimental Program and Fuel Gas Composition

Two sets of experiments were carried out: in the first one, the amount of initial sand used was increased from 15, 30, 45 to 60 g. For the second set of experiments the total amount (mass) of initial bed material was kept constant at 60 g, while 2.5, 5 and 15 g of sand were replaced by char (Coalite, see 3.3, page 87). Experiments were carried out at atmospheric pressure with GL as fuel. Fuel was gasified at 850°C in 10%O₂/CO₂ (O/C = 0.2). The resulting fuel gas composition and carbon conversion are summarised in Figure 34. Coalite was prepared in the size range of 200-300 µm using the same method described in 3.3, page 87, for the fuel preparation. Once graded to the required size range the coalite was mixed with sand until the material appeared to be homogeneous.

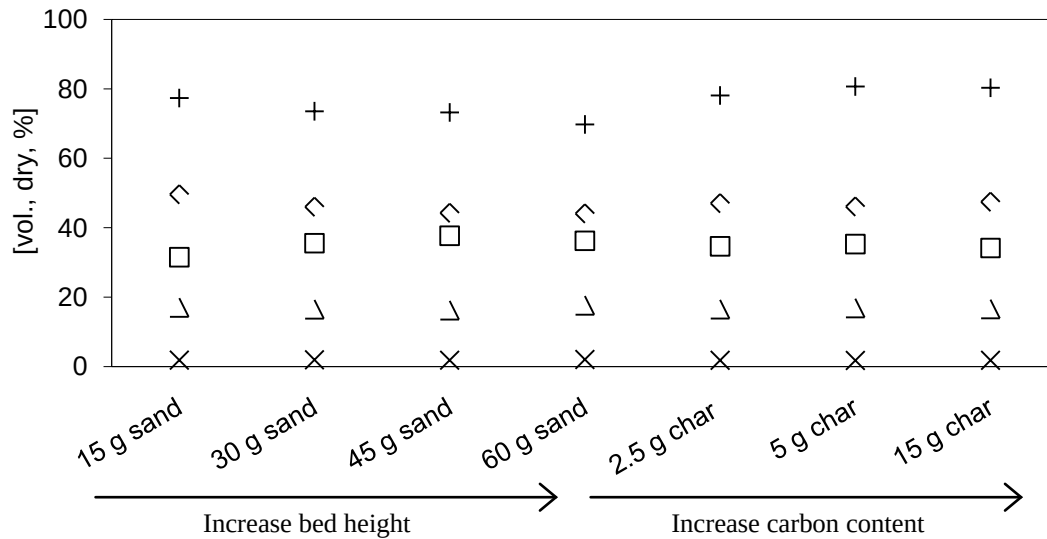


Figure 34: Oxy-fuel gasification of German lignite with different initial bed carbon content and different initial bed size. (□ CO, ◇ CO₂, Δ H₂, × CH₄, + Carbon Conversion [%])

5.2.3 Discussion

5.2.3.1 Gasification Reaction and Carbon Conversion

Bed Height: Analysis of the fuel gas composition and the resulting carbon conversion in Figure 34 shows that increasing the amount of sand used as bed material from 15 to 60 g decreases the carbon conversion from 88% to 70%. This is the opposite of what was expected, based on decreasing residence time and solid back mixing with decreasing bed height. Analysing the bed material recovered after each run it was observed that the carbon/sand ratio in the bed decreases with increasing amount of initial bed material. That is logical as the amount of sand in the bed stays constant throughout the experiment and only depends on the initial amount, while char is constantly added during the experiment as result of incomplete char conversion. It is feasible to assume that the char/sand ratio in the bed with the different quantities of initial bed sand is causing the change in carbon conversion. It has to be noted that the change in carbon conversion is small compared to the error (+/- 8%). However the trend in carbon conversion is consistent with the trend in the fuel gas composition: increasing carbon conversion means also increasing CO/CO₂ ratio. Therefore it can be assumed that the trends seen in carbon conversion are significant.

Carbon content: Figure 34 shows that with increasing carbon content of the initial bed the carbon conversion increases. However this is only true for the increase from 0 to 2.5 g. In subsequent experiments in which the 5 and 15 g of sand were replaced with char, a similar

carbon conversion and fuel gas composition was recorded. The result of this set of experiments leads to the same conclusion as the previous one: increasing char/sand ratio increases carbon conversion. However the existence of an upper limit to this effect is additionally established. The key findings are summarised in Figure 35. The reason behind the increase is not likely to be related to the fact that more carbon in the bed means more carbon can be gasified. Rather it is thought that a certain amount of carbon is improving the mixing, volatile cracking and gas solid contact in the bed. In addition, it is possible that inorganic compounds of coal have a limited catalytic effect on the gasification reactions.

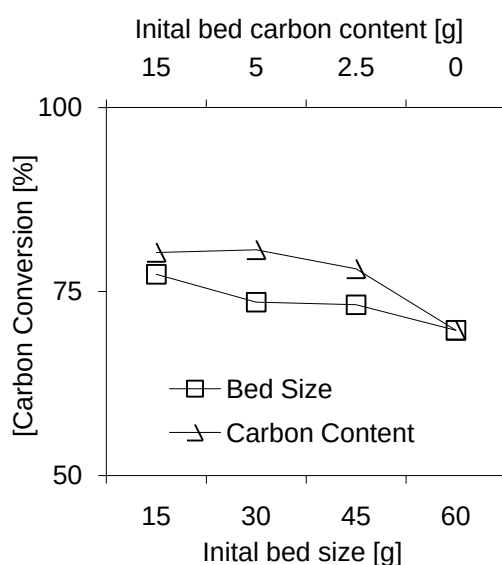


Figure 35: Oxy-fuel gasification of German lignite with different initial bed carbon content (results of set I) and different initial bed size (result of set II).

5.2.3.2 Hydrogen Conversion and Product Distribution

From the fuel gas composition in Figure 34 it can be seen that the amount of H_2 and CH_4 in the fuel gas does not change with bed size or carbon content¹⁸. This is confirmed by the hydrogen product distribution shown in Figure 36. The fraction of CH_4 , H_2O and H_2 in the fuel gas is very similar in all cases. Constant values for hydrogen as CH_4 show that no additional CH_4 is released from coalite, as it is a very low volatile, manufactured fuel and it will have lost all the residual volatiles during start up. As a large fraction of the H_2 and

¹⁸ The hydrogen content of coalite was not included in the calculations

almost all CH_4 is produced during pyrolysis (4.6, page 133) their concentration can be seen as an indication of the heating rate of the fuel particle. Changes in heating rate should change the amount of these gases (2.4.4.3.4, page 54). As mentioned above, the cold test showed maximum solid back mixing occurring with 60 g of bed material. Therefore optimum bed – fuel particle heat transfer (highest heating rate) should occur at this condition while with smaller size beds the heating rate should be slower. This does not seem to be the case, as the CH_4 and H_2 are comparable. It is an indication that the heating of the particle and the subsequent devolatilisation is already happening in the close proximity of the injection spout (i.e. the heating rate must be rapid). At this place the temperature is probably dominated by reaction of the O_2 with part of the fuel and not so much by the heat transfer from the fluidised bed.

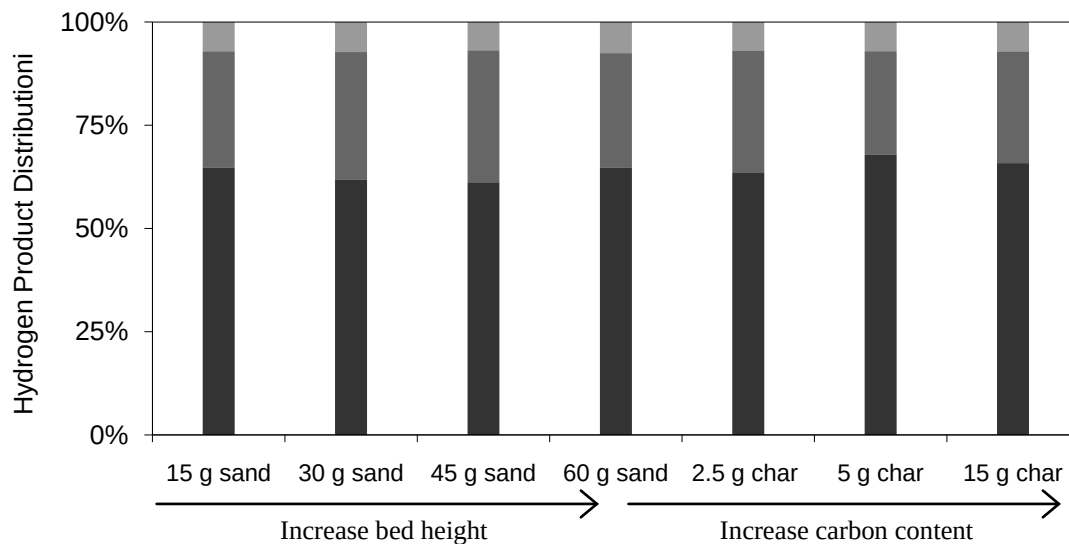


Figure 36: Oxy-fuel gasification of German lignite at different initial bed char content and different initial bed heights – Hydrogen Product Distribution (■ H_2 , ■ H_2O , ■ CH_4).

5.3 Comparing Dolomite and Silica Sand

5.3.1 Background

As discussed in the introduction to this chapter, dolomite is added as bed material to fluidised bed gasifiers for two reasons, sulphur retention and catalytic activity. The potential of retaining sulphur in an O_2/CO_2 blown system is investigated separately in 8.3.5, page 192. In this section the potential catalytic activity and the related improvement in gasification efficiency are investigated. In addition, the agglomeration and partial de-fluidisation under high temperature and with oxygen using a silica sand bed as reported in 4.3.3.3, page 118, makes it necessary to test alternative bed materials. Therefore this discussion begins with an analysis of the operability of the gasifier when dolomite was used in the bed before the gasification characteristics in terms of carbon conversion and fuel gas composition are discussed.

5.3.2 Experimental Program and Fuel Gas Composition

Experiments were carried out at atmospheric pressure with GL. The fuel was gasified at 850°C and 950°C in 10% O₂/CO₂ (O/C = 0.2). For one experiment 3% dolomite was mixed with the fuel and fed together. For the second set of experiments, 20, 40 and 60% of the sand was replaced by dolomite. The total mass of bed material was kept constant (60 g). The resulting fuel gas composition and carbon conversion are summarised in Figure 37. Dolomite was prepared in the size range of 200 - 300 µm using the same method as described in 3.3, page 87 for the fuel preparation. Once graded to the required size range, the dolomite was either premixed with the fuel or mixed with sand. In both cases the required amounts were weighed and thoroughly mixed until the material appeared to be homogeneous.

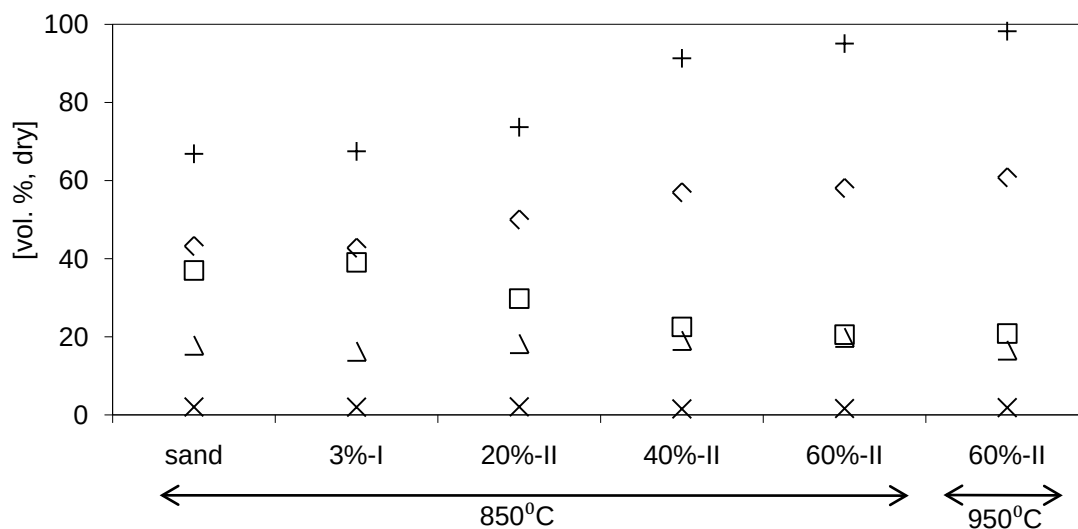


Figure 37 Oxy-fuel gasification of German lignite with different %dolomite/sand mixtures as initial bed (10% O₂/CO₂, atmospheric pressure). (I: co-feeding with the fuel, II: mixed with initial bed material, $\square$ CO, $\diamond$ CO₂, Δ H₂, $\times$ CH₄, + Carbon Conversion [%])

5.3.3 Discussion

5.3.3.1 Gasification Reaction and Carbon Conversion

Operability: Increasing the amount of dolomite in the bed had two major effects on the operability of the reactor: (1) For all experiments with dolomite, a large amount of dolomite fines was found to accumulate in the tar trap and increase the pressure drop through the system. Dolomite particles break up to such an extent that they become entrained in the gas stream. The implication of this was that experiments with dolomite had to be of short duration to avoid large pressure drops and pressure build up. However, in large scale

gasifiers, the gas is separated from most of the entrained particles right after the reactor, using cyclones and therefore this would not be an insurmountable problem. (2) No agglomeration of bed material was observed. As discussed in 4.3.3.3, page 118, a gasification temperature of 950°C and the presence oxygen in the fluidising gas causes agglomeration and partial defluidising in the bed due to lignite ash-sand interaction. For the same experimental conditions except using 60% dolomite/sand as bed material, no agglomeration was detected. This is further supporting the claim that the observed agglomeration is related to silica sand. Experiments with 60% dolomite simply do not contain as much sand and therefore agglomeration is less likely.

Premixing: Mixing 3% of dolomite with the fuel and co-feeding into a preheated sand bed yields a similar carbon conversion and fuel gas composition compared to feeding pure fuel (Figure 38). This is probably due to the relatively low amount of dolomite in the bed. A total of 1 g is injected over the duration of the experiment. This results in a low dolomite/sand ratio compared to the other experiments where a minimum of 12 g dolomite was used in the bed. In addition part of the dolomite is lost as it breaks up and is entrained by the gas flow. Feeding additional bed material together with fuel is common for fluidised bed gasifiers where solids can be constantly removed from the bed. Even if the start up of such a gasifier is with a pure silica sand bed, over time the bed would be replaced by dolomite, ash and char.

Dolomite in the initial bed: Increasing the ratio of dolomite/sand of the initial bed increases carbon conversion from 70% for experiments with pure sand beds to 90-95% for experiments with 40 - 60% dolomite/sand beds. The other data relevant for the process performance are shown in Figure 38. Using 60% dolomite increased the LHV of the produced fuel gas from 8.5 to 10.5 MJ/m³ and the energy conversion to 100%. Analysing the CO₂ conversion (see 4.4.3.1, page 122) it can be seen that it increased from 30 to 50%. This shows clearly that the rate of char-CO₂ reaction increases with dolomite in the bed. Catalytic activity of CaO towards the char-CO₂ and char-steam reaction is well known and a possible catalytic surface mechanism was discussed in 2.4.5, page 57. As mentioned before, dolomite particles tend to break up and are therefore available in the bed as fine dust probably covering the coal particle to a certain degree before being entrained in the gas flow. This would be necessary for them to be active as catalyst. It is seen from the data, that a dolomite/sand ratio of 0.4 in the bed is enough under these conditions to obtain the best process performance. Further increasing the content of dolomite in the bed has no or only very limited effect on the process.

Interestingly the results show a similar trend as established in 4.6, page 133: under selected conditions (adding 25% steam, high CO_2/C ratio and more than 40% dolomite in the bed) the carbon conversion and therefore the process performance at 850°C is comparable to the one at 950°C (Figure 38). For the experiments carried out here, the heat required was provided externally. In a larger scale operation the difference between 850°C and 950°C would be a larger consumption of oxygen and more CO_2 in the fuel gas at the higher temperature. This would overall lead to a lower efficiency of the process taking into account that complete carbon conversion can already be achieved at 850°C .

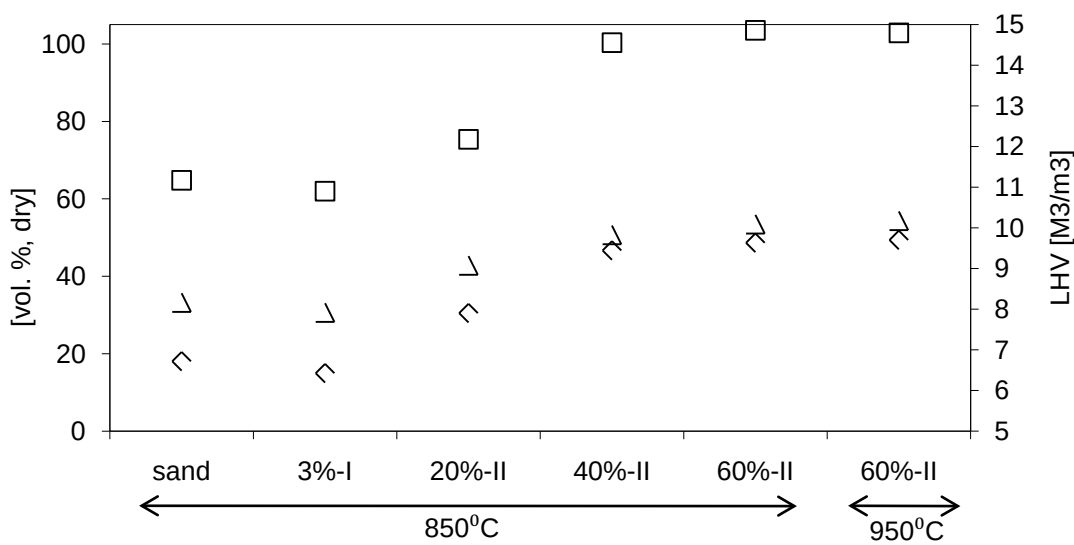


Figure 38: Oxy-fuel gasification of German lignite with different dolomite/sand mixtures as initial bed (10% O_2/CO_2 , atmospheric pressure) (□ Energy Conversion [%], ◇ CO_2 conversion, Δ LHV).

5.3.3.2 Hydrogen Conversion and Product Distribution

The hydrogen product distribution for this set of experiments is shown in Figure 39. The amount of hydrogen as CH_4 in the fuel gas does not change for different gasification conditions as it is mainly produced during pyrolysis and does not participate in further gas phase reactions. This is a result similar to the one discussed in detail in 4.6, page 133. Comparing the amount of hydrogen as H_2 and H_2O in the fuel gas two trends can be established: (1) increasing the amount of dolomite increases the $\text{H}_2/\text{H}_2\text{O}$ ratio (2) increasing the gasification temperature from 850°C to 950°C decreases the $\text{H}_2/\text{H}_2\text{O}$ ratio. Both effects can be related to the WGS reaction. Increasing amount of dolomite increases carbon conversion and partial pressure of CO . Therefore the WGS equilibrium shifts towards H_2 and

the amount of H_2O in the fuel gas decreases. Increasing the temperature under otherwise comparable conditions (mainly similar amount of O, C and H in the gas phase), shifts the gas phase equilibrium towards H_2O as the WGS reaction is slightly exothermic.

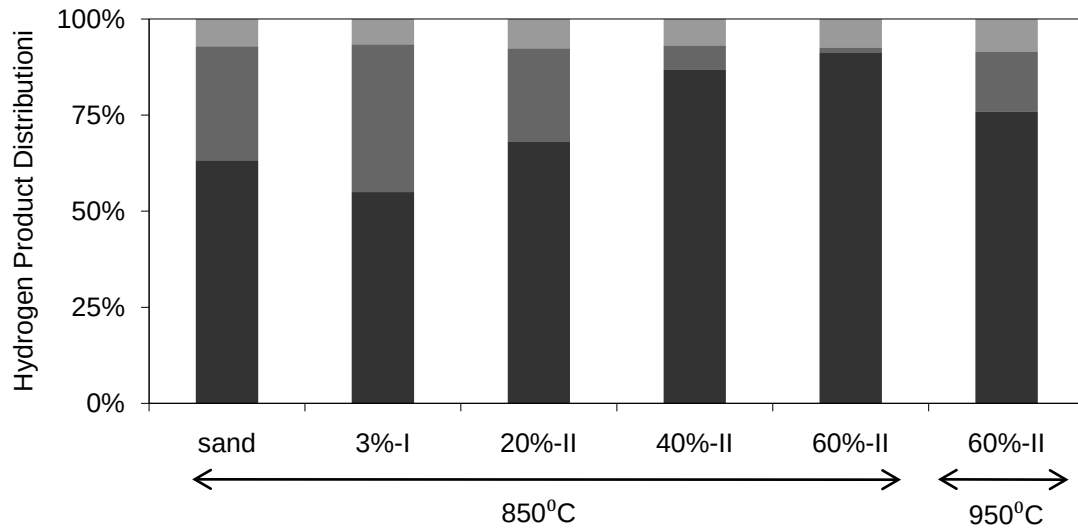


Figure 39: Oxy-fuel gasification of German lignite at different temperatures and dolomite content of the bed/feed – Hydrogen Product Distribution (■ H_2 , ■ H_2O , ■ CH_4).

5.4 Summary

The main aim of the summary in this chapter is to see if the questions asked in the beginning can be answered based on the results discussed and what conclusions can be drawn from them.

- (1) What is the influence of the bed height on the gasification performance? And does the increasing bed height (increasing gas residence time) increase the carbon conversion?

No relationship between increasing gas residence time (bed height) and increasing carbon conversion could be identified as the results actually showed the opposite trend. The condition with the most dominating influence on the carbon conversion is probably the sand/char ratio in the bed, and this ratio increases with decreasing initial bed height. Residence time and improved solid back mixing have no or only a much smaller influence on the gasification performance. The main conclusion is that increasing the bed height does not seem to be a feasible way to increase the carbon conversion. The deactivation of char over time prevents it from being effective. However these results are based on the experiments carried out in a small scale reactor (28 mm). In a large scale commercial reactor the situation could be different.

- (2) How is the char content of the bed influencing the gasification performance?

The char content of the bed seems to have a strong influence on the gasification performance. Both sets of experiments, varying bed height and initial char content, showed a clear trend. Increasing char content increases carbon conversion. In addition, it was found that there is an upper limit to the improvement in carbon conversion. It is rather difficult to identify a single reason for this effect. The overall gasification performance probably increases due to better bed mixing, increased gas char contact, enhanced volatile destruction and potential catalytic effect of the ash.

- (3) What are the differences of silica sand and dolomite as bed material?

The outcome of this set of this experiment can be summarised as follows: No bed agglomeration and increased extent of char gasification are observed with a dolomite

bed compared to a silica sand bed. In addition, it was found that dolomite particles tend to break up quickly in the bed and get entrained in the gas flow. The char- CO_2 reaction was fast enough to convert all carbon at 850°C and 950°C. Increasing temperature only affected the WGS equilibrium in the gas phase and the ratio of H_2/CO was lower at higher temperatures.

6 Gasification under Elevated Pressure

6.1 Introduction

Large scale gasifiers tend to be operated at elevated pressure. The main advantages are increased throughput, smaller equipment size and higher process efficiency by improved integration with downstream processes. Increasing the total pressure in a chemical conversion process has a significant influence on every aspect of the process. In this chapter the influence of increasing pressure on the gasification performance is investigated.

In addition to the results obtained from the fluidised bed reactor (FBR) a high pressure wire mesh reactor (WMR) was used to produce data for comparison¹⁹. Therefore the chapter starts with a brief description of the WMR and its capabilities. The next section gives an overview of the experimental program and the selected operating conditions used in both reactors. First the effect of pressure on pyrolysis yields for the FBR and WMR are discussed, before the effect on gasification performance is described. The main effect of increasing gasification pressure was found to be a decrease in carbon conversion. Therefore WMR results plus optical microscopy and electron microscopy were used to analyse the char morphology changes leading to this decrease in gasification efficiency. The last section in this chapter discusses how the carbon conversion at elevated pressure can be improved by changing the gasification agent and gasification temperature. The aim is to develop strategies to optimise gasification performance, which can then be used to assist in the design of a pilot oxy-fuel installation working at elevated pressure. The operating parameters were changed, based on the fundamental understanding gained from the analysis of the performance under atmospheric pressure (4, page 108). A decrease in the carbon conversion was identified as the main effect of increasing pressure and therefore carbon conversion is used to judge the gasification performance.

The results in this chapter are produced using a specific feature of the bench scale reactor: due to its relative small scale it is possible to investigate the influence of a single variable, in this case pressure, on the gasification performance, while keeping the other parameters

¹⁹ The WMR work was carried out by Dr. Cesar Berruero (c.berruero@imperial.ac.uk) in this laboratory.

constant. In a larger scale test facility that would not be possible as they are designed for a fixed set of operating parameters and these are interrelated.

6.2 Wire Mesh Reactor

A wire mesh reactor for pyrolysis and gasification experiments was developed over several years at Imperial College London. The wire mesh reactor allows the investigation of the thermal breakdown of fuels under a wide range of conditions. It allows the study of single-particle behaviour as the influence from the reactor design on the results is minimal. The design and operation of the reactor are described elsewhere in detail [62, 159, 160]. Here only a brief description of the reactor and its capabilities is given: 5 - 6 mg of fuel is placed between two layers of wire mesh (stainless steel mesh for experiments with He, molybdenum mesh for CO₂). The mesh is placed between two electrodes serving as sample holder and resistance heater. The reactor allows accurate control of heating rates (up to 10,000°C/s) and holding time. Experiments can be carried out at temperatures up to 2000°C and 100 bar. During operation, a stream of gas flows through the sample holder, removing volatiles away from the vicinity of the reaction zone into a tar trap cooled with liquid nitrogen for experiments with He and with dry ice in the case of CO₂ [73].

The influence of pressure on the pyrolysis and gasification of coal was extensively studied, as well as the influence of reactor configuration on the results [70]. It was found that for the batch operation of the FBR, the results were consistent with those obtained using the WMR. This showed that the heating rate in the FBR reactor is in the range of 1000°C/s and that the batch coal samples are properly separated upon injection into the bed. However due to the tar cracking in the bed and the freeboard of the FBR, tar quantities and composition were altered compared to the WMR. An overview of the previous work and a summary of the key findings are presented in 2.4.4.3, page 53. For this study, results from the WMR are compared to those obtained with the continuously fed FBR under steady state conditions. Figure 40 shows the schematic diagram of both reactors and their main differences. In the WMR, a batch coal sample is heated at 1000°C/s to the desired temperature and kept at this temperature for a defined holding time. Any volatiles released from the particles are immediately swept away by the gas stream and condensed in the tar trap. The weight change of the particles and the tar trap are measured. In the FBR, coal is fed continuously into preheated sand. Volatiles released have to pass through the bed and free board before gas stream is cooled to ambient

temperature. The fuel gas composition and the fuel feeding rate are measured. The solid particles remain in the bed over the whole duration of the run.

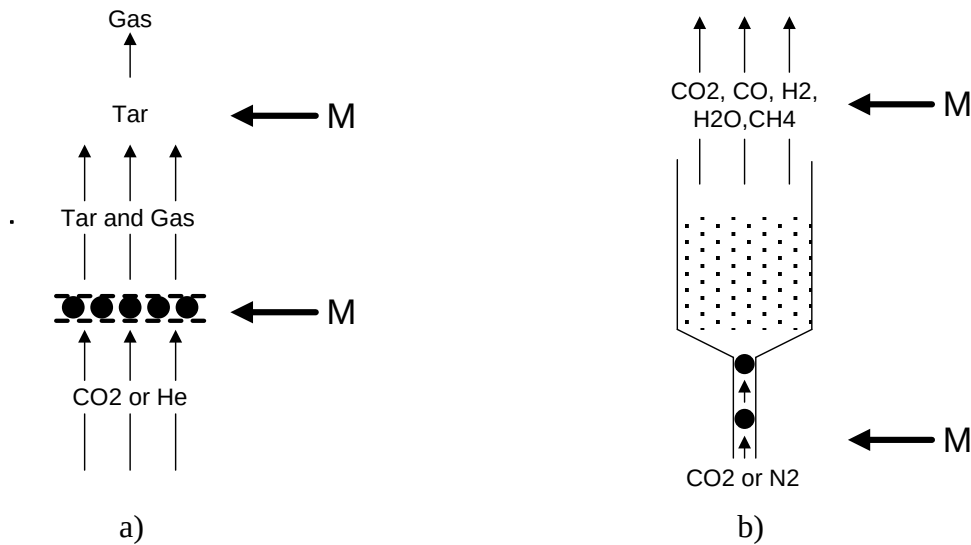


Figure 40: Schematic diagram of the fuel particles, gas streams and points of measurement (M) in a) wire mesh reactor b) semi-continuous operated fluidised bed reactor.

6.3 Overview over the Experimental Program

FBR: For all experiments GL was used as the fuel. The pressure range from 5 to 20 bar was selected, as in this range it was possible to keep the ratio between fuel, fluidising agent, oxidiser and the superficial velocity constant. The experimental conditions for the basic set of experiments are summarised in Table 13 and the experimental program is shown in Table 14. A lower superficial velocity (0.08 m/s) than those used under atmospheric conditions (0.1-0.2 m/s) had to be selected in order to keep it constant over the pressure range investigated. For experiments with oxygen the gasification agent was 3.7%O₂/CO₂ and in case of steam addition, 15% steam/ 3.7% O₂/ CO₂ (O/C ratio = 0.2). Different CO₂/C ratios were achieved by changing the flow of CO₂ and keeping the feed rate constant. As already discussed in 4.4, page 121, this keeps the contribution from pyrolysis constant, while changing the gas velocity (for a discussion on the influence on superficial velocity see: 3.5, page 98). A considerable amount of testing was required to carry out experiments under elevated pressure with continuous feeding. This included several unsuccessful runs before stable operation conditions could be achieved and the fuel gas could be analysed under steady state conditions.

Table 13: Overview of the experimental conditions for the FBR.

Pressure [bar]	FFR [g/min]	F [l/min]	U_s [m/s]
5	1.5	4	0.08
10	3.0	8	0.08
15	4.5	12	0.08
20	6	16	0.08

Table 14: Experimental program carried out with the fluidised bed reactor under elevated pressure (x: experiments carried out under these conditions; diff. CO₂/C: experiments with different CO₂/C ratio carried out under these conditions)

Temp. [°C]	Gas	5 bar	10 bar	15 bar	20 bar
850	N ₂	x	x	x	x
850	CO ₂	x	x	x	
850	O ₂ /CO ₂	diff. CO ₂ /C	diff. CO ₂ /C:	diff. CO ₂ /C:	x
850	Steam/O ₂ /CO ₂	x	x	x	
950	O ₂ /CO ₂	x	x		

WMR: The experimental program is summarised in Table 15. For the pyrolysis experiments He was used. Gasification was carried out with pure CO₂. Experiments were repeated where necessary.

Table 15: Experimental program carried out with the wire mesh reactor in the pressure range 1 – 20 bar (x: experiments carried out under these conditions; diff. HT: experiments with different holding times carried out under these conditions).

Temp. [°C]	Gas	d_p [μm]	1 bar	5 bar	10 bar	15 bar	20 bar
850	He	106-150	x	x	x	x	x
950	He	106-150	x				x
850	CO ₂	150-205	x	diff. HT	diff. HT	x	x

6.4 Pyrolysis

6.4.1 Background

Elevated pressure is known to suppress the release of volatiles from the fuel particles. Rather than being released, tar molecules can deposit inside the pore structure of the particles and build a layer of unreactive secondary char. This layer of unreactive char reduces the overall char reactivity of the particles. In the gas phase, increasing pressure promotes the formation of CH_4 from H_2 and CO .

6.4.2 Discussion

The fuel gas composition during the pyrolysis of GL at elevated pressure is shown in Figure 41. The concentration of CO (6%) and H_2 (10%) is fairly constant over the investigated pressure range, while the concentration of CH_4 and CO_2 in the fuel increased. As mentioned above, the formation of CH_4 is favoured by higher pressure. Pressure also affects the Boudouard equilibrium shifting it to higher CO_2 concentration.

Figure 43 shows the gas yield for the continuously fed FBR, calculated from the fuel gas flow rate and the fuel gas composition, and the tar, gas and total volatile yield for the WMR. Three main observations can be made on the effect of increasing the total pressure: (1) The WMR tar yield decreased slightly. (2) The WMR gas yield increased slightly and the change was consistent with the tar yield decrease. (3) The WMR total volatile yield and the FBR gas yield were very similar and had a relatively flat profile over the pressure range. Tar suppression with increasing pressure is well documented as mentioned above. The increase in gas yield in the WMR can be explained by part of the tar cracking on the pore walls, before the resulting larger molecules condensed to form the secondary char. Similar values for the FBR and WMR (range 50 - 60%) for the total volatiles released indicate that under steady state conditions the large majority of the tar in the FBR is cracked effectively in the bed and the freeboard. In previous studies [73] the tar content measured in the batch fed FBR was lower than for the WMR, but still significant. However those experiments were carried out with a sand bed, while the steady state gas composition, used as the basis for calculating the data in this work, was measured with a bed containing char (> 10 g). This is likely to increase the extent of char cracking²⁰. Three main conclusions that can be obtained from this analysis:

²⁰ The effect of the char content in the bed on the tar cracking is discussed in more detail in 8.2.2, page 171.

Firstly, the WMR can successfully predict the gas yield from the continuously fed FBR under pyrolysis conditions. Secondly, all of the tar released in the FBR is cracked in the bed. Thirdly, the gas yield is fairly constant over the pressure range in both reactors.

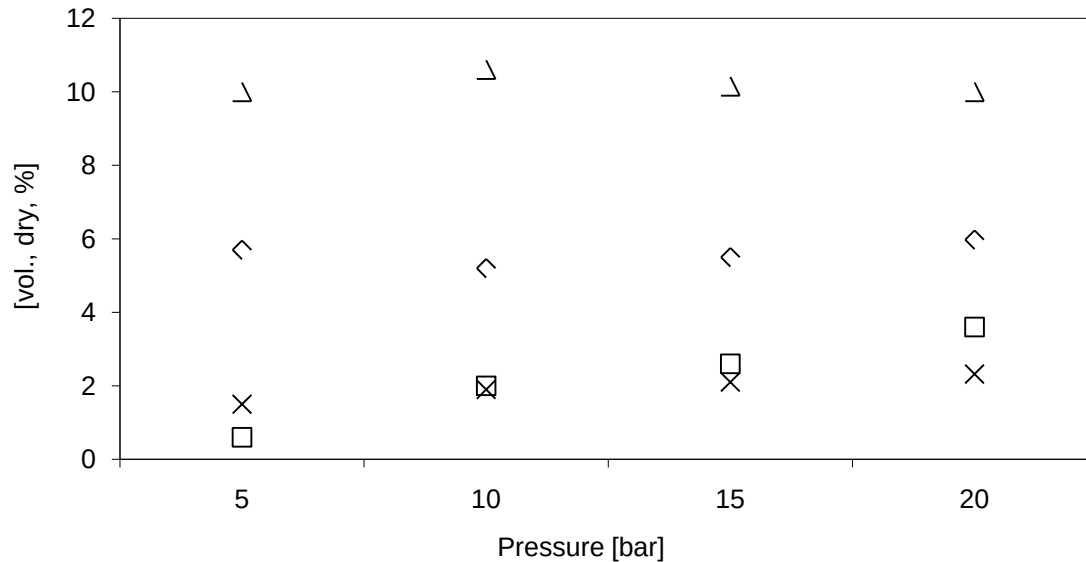


Figure 41: Pyrolysis of German Lignite at 850°C with N₂: Fuel gas composition (□ CO₂, ◇ CO, Δ H₂, × CH₄).

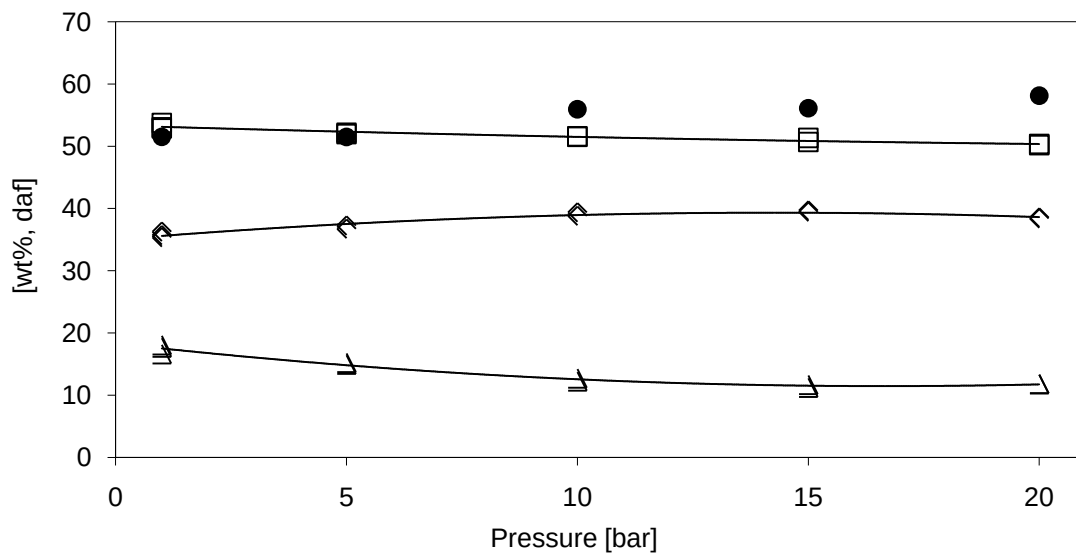


Figure 42: Pyrolysis of German Lignite at 850°C: Comparison. WMR: Δ Tar yield, ◇ gas yield, □ total volatile. FBR: ● Gas yield

6.5 Gasification

6.5.1 Background

The effect of increasing gasification pressure was intensively studied (review of previous studies: 2.4.4.3.3, page 54) using batch reactors with different configurations. Three main effects were identified in these studies: (1) Suppression of volatile release (2) resulting in decrease in char combustion reactivity with increasing pressure and (3) an increase in extent of char gasification with increasing pressure. These key points are used as a basis for the discussion of the experimental results.

6.5.2 Discussion

The discussion of the results is split into two sections. In the first section the influence of pressure on the fuel gas composition, carbon conversion and the hydrogen product distribution is investigated using the results from the FBR, WMR and optical analysis of the char particles. The discussion in the second section focuses on improving gasification performance at elevated pressure. For the optimisation of the gasification performance, the trends established at atmospheric pressure are used as a basis for discussion.

6.5.2.1 Effect of Pressure

A set of dedicated experiments was carried out to investigate the effect of pressure. In order to produce comparable results, the fuel gas feeding rate and the solid/gas ratios were kept constant. The superficial velocity and the fuel feeding rate are comparable to those used in the pyrolysis experiments. First the trends with pressure (fuel gas composition and hydrogen distribution) are described, while in a second step the underlying conditions are analysed in more detail (comparing carbon conversion in the WMR and FBR and optical char analysis).

Fuel gas composition and hydrogen distribution in FBR: The fuel gas composition during the gasification of the GL gasification at elevated pressure is shown in Figure 43 and the hydrogen product distribution in Figure 44. With increasing pressure the concentration of CO₂ increases (60 to 70%), while CO decreases (30 to 20%). At the same time less fuel-hydrogen was converted to H₂ (43 – 30%) and more to H₂O. The concentration of CH₄ in the fuel gas increased slightly with pressure, but this is thought to be an effect of the changing fuel gas flow rate rather than a change in total amount of CH₄ released (constant fuel-hydrogen to CH₄ conversion of 6-8% in Figure 44). This indicates that CH₄ is mainly formed during pyrolysis and not by the gas phase reaction (reverse steam reforming). It also shows

that the conversion of H_2 to CH_4 with increasing pressure is not the reason for the change in fuel-hydrogen to H_2 conversion. It rather seems that the extent of char-steam reaction (steam from fuel moisture) decreases with pressure. The decreasing CO/CO_2 ratio of the fuel gas indicates the same trend: decreasing extent of char-gas reaction.

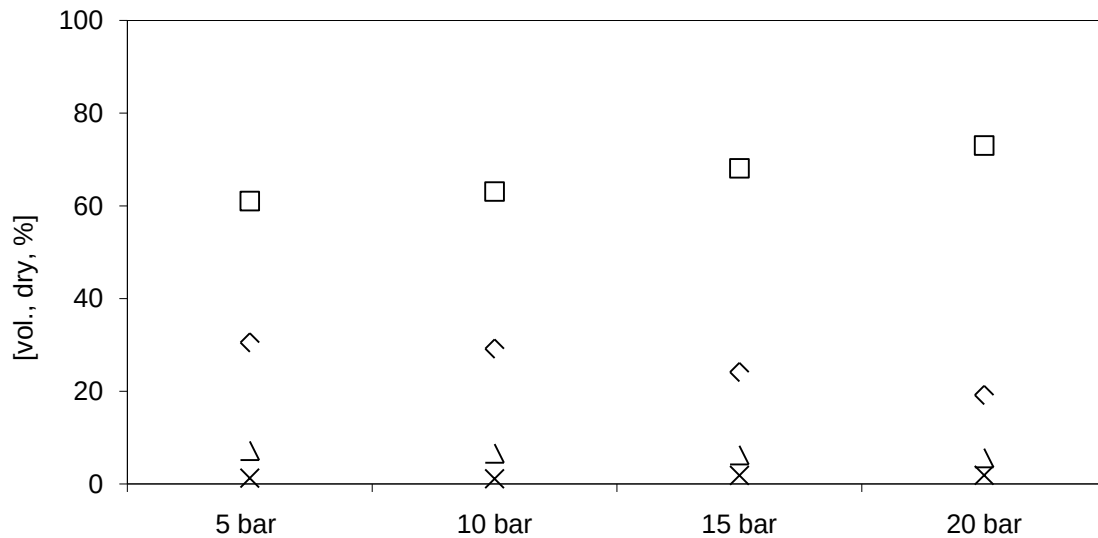


Figure 43: Oxy-fuel gasification of GL at 850°C with 3.7% O_2/CO_2 ($O/C = 0.1$) at different pressures: Fuel gas composition ($\square$ CO_2 , $\diamond$ CO , Δ H_2 , $\times$ CH_4).

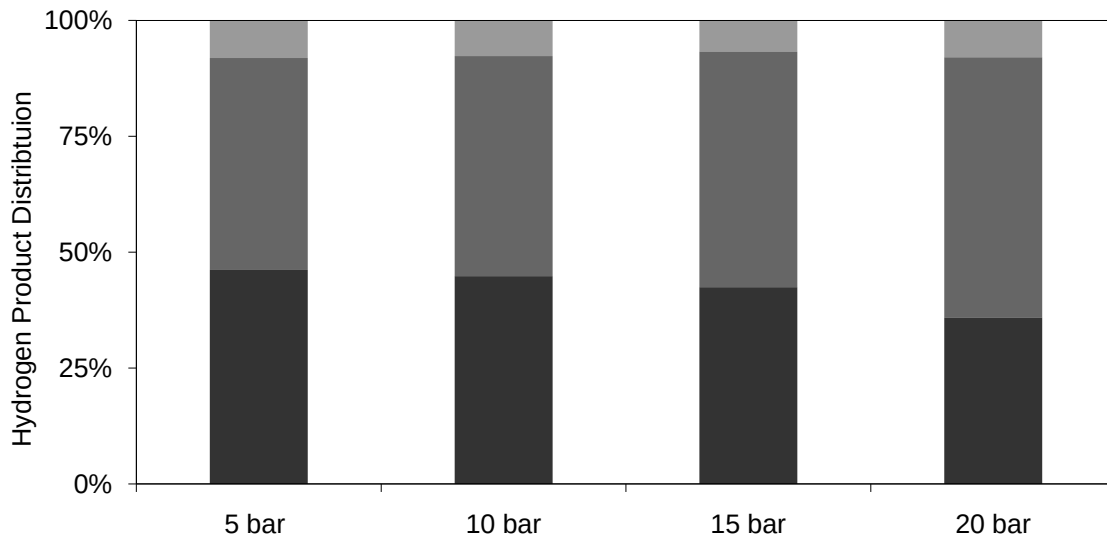


Figure 44: Hydrogen product distribution: Oxy-fuel gasification of German Lignite at 850°C with 3.7% O_2/CO_2 ($O/C = 0.1$) at different pressures: Hydrogen Product Distribution ($\blacksquare$ H_2 , $\blacksquare$ H_2O , $\blacksquare$ CH_4).

Carbon Conversion in FBR and WMR: The decrease of the CO/CO₂ ratio in the fuel gas with increasing pressure is a result of the decreasing carbon conversion due to a decreasing extent of gasification. (Figure 45: from 73% at 5 bar to 54% at 20 bar). This does not correspond with increasing extent of gasification with pressure observed by previous studies using the batch fed FBR and can also not be explained by the suppression of the volatile release during pyrolysis as this is only 3% as established before. Figure 45 shows a direct comparison of the carbon conversion measured in the WMR and FBR. The differences in the experimental conditions between the two reactors were discussed above. It can be seen that up to 10 bar the results are comparable. The conversion in the WMR is 10% higher than in the continuously fed FBR for 60 s holding time, while for 10 s holding time the results are very similar. In the range from 10 to 20 bar, the carbon conversion in the WMR increases slightly (discussed above) while for the FBR reactor the conversion decreased sharply. From these results, it can be concluded that the fuel particles injected into the FBR form chars which lose their reactivity much quicker than predicted by the WMR. After 10 s, the char particles in the FBR are uncreative. This effect seems to increase in importance with increasing pressure.

Optical char analysis: In order to explain the decrease in carbon conversion, the char morphology was analysed using an optical and an electron microscope (EM). Figure 46 shows images of FBR char particles taken with an optical and with an electron microscope. The first column shows: optical pictures from char particles recovered after pyrolysis in the pressure range from 1 - 15 bar, while the second column: char particles from gasification. Two observations can be made: Firstly, pyrolysis char particles have a more reflecting surface than gasification char. Secondly the number of char particles with reflecting surface seems to increase with increasing pressure for the gasification chars. The EM micrographs of the gasification chars with increasing pressure are shown in the third column. The most obvious difference can be found comparing 1 bar and 5 bar. While at 1 bar the char seem to be very porous and the pore size is rather small, at 5 bar the pore size is much bigger. At 10 and 20 bar, the surface looks like solidified bubbles (marked with white arrows). With increasing pressure the release of tars is suppressed and bubbles are formed and solidify within the forming char particles. The passage of the volatile vapours to the particle surface creates pores. Tar released by these bubbles seem to re-condense on the char surface and covering it with a layer of secondary char seen as the reflecting surface with the optical microscope.

Conclusions: The carbon conversion in the FBR decreased with increasing pressure. This effect could not be predicted from the WMR data and was not observed in previous studies when a batch fed FBR was used. Up to 10 bar, FBR conversion is comparable to conversions at 10 s holding time in the WMR. Optical analysis shows a structural change in the char surface with increasing pressure. The number of pores decreased and their size increased. The surface seems to have become more and more coated by secondary char as the pressure was increased. One reason for the decrease in conversions could be the suppression of volatile release with increasing pressure however this effect should be the same in the WMR reactor and can therefore not explain the results. However there is a major difference between the two reactors. For the WMR the amount of fuel used for experiments at each pressure was very similar (approximately 5 mg) and fuel particles are segregated from each other. For the FBR, the fuel feed rate was increased with pressure to keep the gas/fuel ratio constant (1.5 g/min at 5 bar to 6 g/min at 20 bar). That means that the amount of fuel particles in the spout line and at the injection point is 4 times higher at 20 bar. As a result, the particles became more concentrated and closer together with increasing pressure compared to the batch fed operation. An increase in particle-particle interaction at higher fuel pressure could therefore be expected. The possible effects of this were: (1) Tar released from one particle could condense on another one and build a layer of secondary char, decreasing the char reactivity. (2) The mixing of fuel particles with the hot bed material was reduced, reducing the particle heating rate and char reactivity

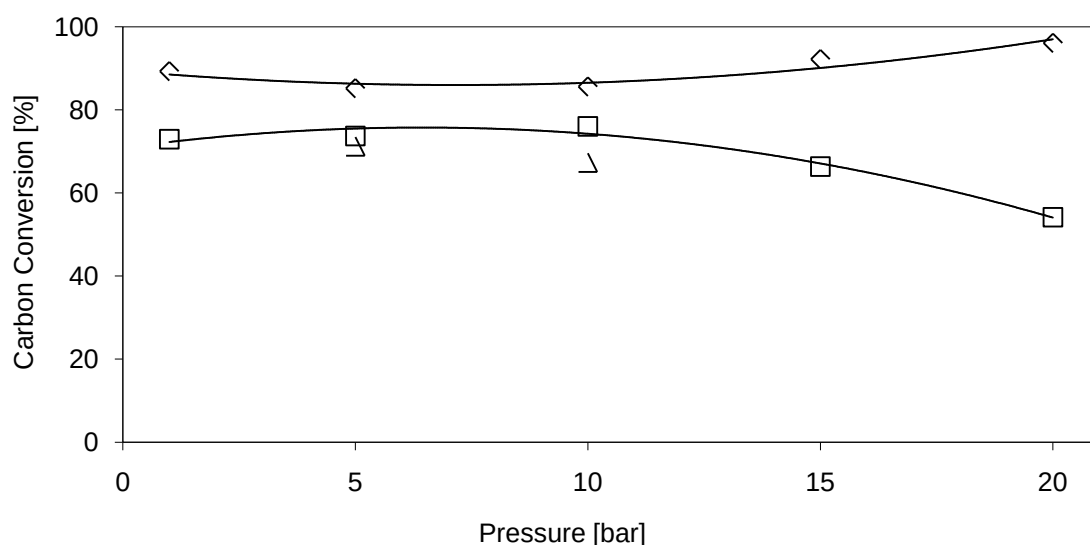


Figure 45: Carbon Conversion. WMR: 850C-CO₂, Δ 10 s and ◇ 60 s holding time. FBR: □ 850C-O₂/CO₂.

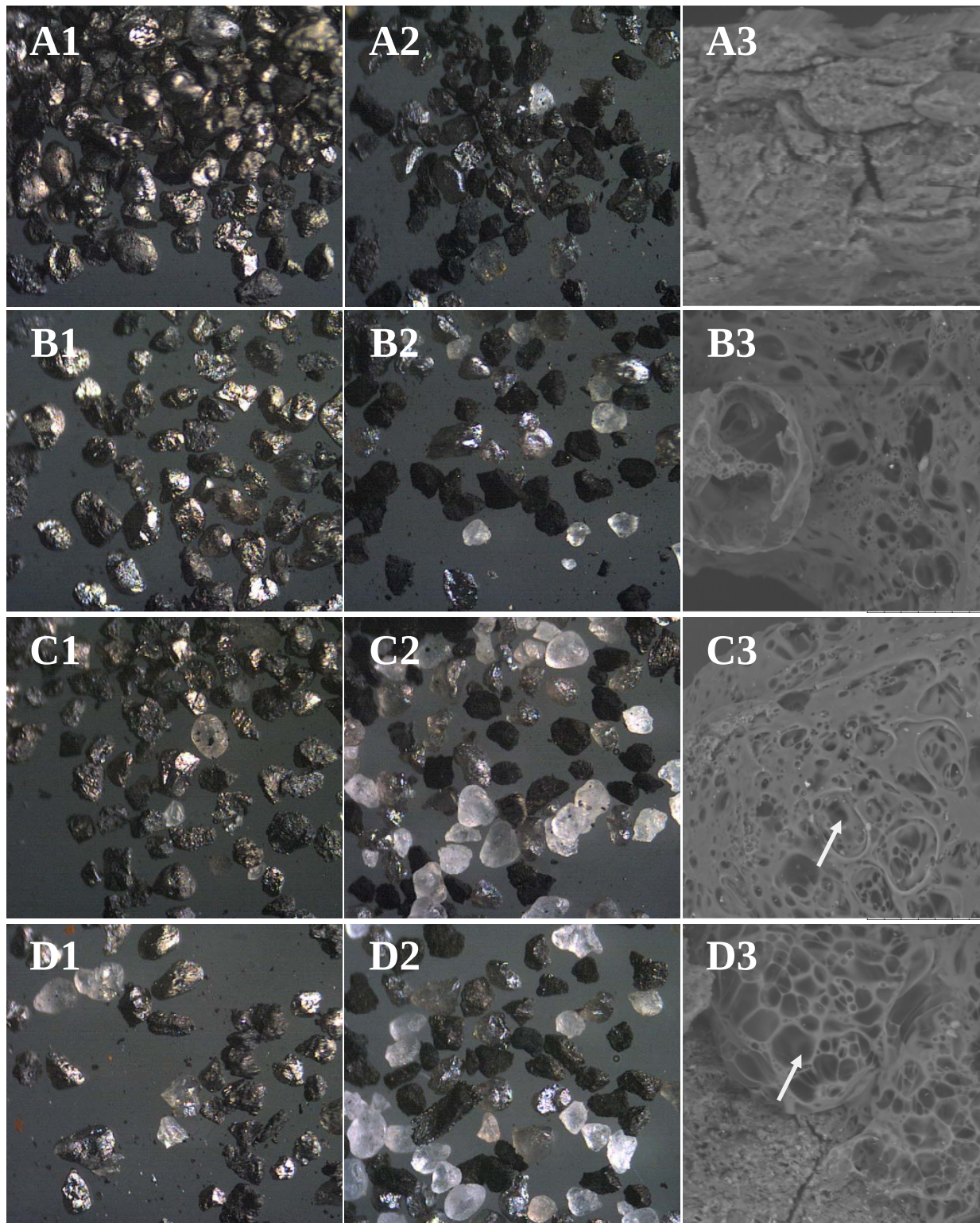


Figure 46: Picture of the bed material recovered after the experiments at different pressures (A – 1 bar, B – 5 bar, C – 10 bar, D – 15 bar). Optical microscope, 4x: column 1 – pyrolysis experiments, column 2 – gasification experiments. EM pictures, 1000x: column 3 – char particles from gasification experiments.

6.5.2.2 Optimising Gasification Performance

The effect of gasification conditions on the gasification performance is discussed in detail in Chapter 4, page 108, for operation under atmospheric pressure. The trends identified there, were used to increase the performance under elevated pressure. They consisted of:

- (1) Adding oxygen (shown in Figure 47)
- (2) Adding steam (shown in Figure 47)
- (3) Increasing gasification temperature (shown in Figure 47)
- (4) Increasing CO₂/C ratio - Figure 48 and Figure 49

The change in carbon conversion is used to judge the gasification performance.

Adding oxygen: The carbon conversion for gasification with pure CO₂ is not complete (5 and 10 bar, approximately 60% carbon conversion). Operating with 3.7% O₂/CO₂ (O/C ratio = 0.2) increased the carbon conversion to approximately 75% at 5 and 10 bar, as under these conditions all O₂ is reacting (Figure 47). However, in a large scale plant, oxygen would always be added to combust part of the fuel and produce the energy required for the gasification. Levels of oxygen required for a process are mainly determined by the desired operating temperature and process heat requirements (heat load of inputs, heat losses, reaction heat requirements). Therefore the possibilities to raise carbon conversion at industrial scale by varying the O₂ concentration are limited.

Steam addition: Replacing part of the CO₂ with steam was identified in 4.5, page 128, as an option to reduce the gasification temperature from 950°C to 850°C, while maintaining the gasification performance. For experiments at 5, 10 and 15 bar, 15% of the CO₂ was replaced by steam. This resulted in a 10% increase in carbon conversion due to the faster char-steam reaction (Figure 47). Any steam required for the gasifier has to be either produced by an external boiler or by heat recovery, causing extra energy and capital costs or reducing the amount of steam for the steam turbine in the combined cycle. Therefore, the feasibility of steam addition is subject of plant optimisation and techno/economic studies.

Gasification temperature: For 5 and 10 bar the gasification temperature was raised from 850°C to 950°C. This increased carbon conversion from 75% to near completion (Figure 47).

It was not possible to operate the gasifier at 15 and 20 bar and 950°C as sufficient heat could not be provided by the resistance heater. Increasing gasification temperature required more oxygen and reduces the overall energy conversion efficiency to fuel gas, as more fuel is converted to CO₂. However maximum carbon conversion is necessary to ensure the economic operation of large plants and therefore a high operating temperature is favourable.

Increasing CO₂/C ratio: The CO₂/C ratio was varied over a wide range for 5 bar and selected experiments were carried out at 10, 15 bar with different CO₂/C ratios. The ratio is changed by changing the amount of CO₂ injected into the reactor and keeping the coal feed rate constant. In this way, the contribution of pyrolysis is similar for each experiment. The gas velocity in the reactor changes but at the small scale this does not have a significant effect. As established in 4.4, page 121, for operation under atmospheric pressure, the carbon conversion increases with increasing CO₂/C ratio. For the case of 5 bar, carbon conversion reached 100% for a CO₂/C ratio > 4. The same trends were confirmed for 10 and 15 bar and the extrapolated trend is shown for 20 bar. However increasing the CO₂/C ratio diluted the fuel gas with CO₂, decreasing its heating value from 8 to 4 MJ/m³. Furthermore the additional volume gas injected into the reactor in a large scale plant would require more energy, as the gas stream has to be heated to gasification temperature. In addition, if the CO₂/C ratio is adjusted to 4, the gas cleaning, the recycle loop and especially the compressor before the gasifier need to handle a large gas volume. This certainly reduces the overall plant efficiency.

The results of varying operating conditions on the carbon conversion followed the trends established for operation under atmospheric pressure. The trends established under elevated pressure provide a good basis for selecting operating conditions for a larger scale plant. It seems that at elevated pressure and increased fuel feeding rate, the reactivity of the gasification process needs to be increased in order to achieve a gasification performance comparable to atmospheric pressure. In the laboratory scale reactor this could either be done by increasing the gasification temperature, replacing part of the CO₂ with steam or increasing the CO₂/C ratio. In a large scale plant it is not possible to vary a single variable independently, therefore a combination of these strategies together with adjusting the amount of oxygen would be the most likely option.

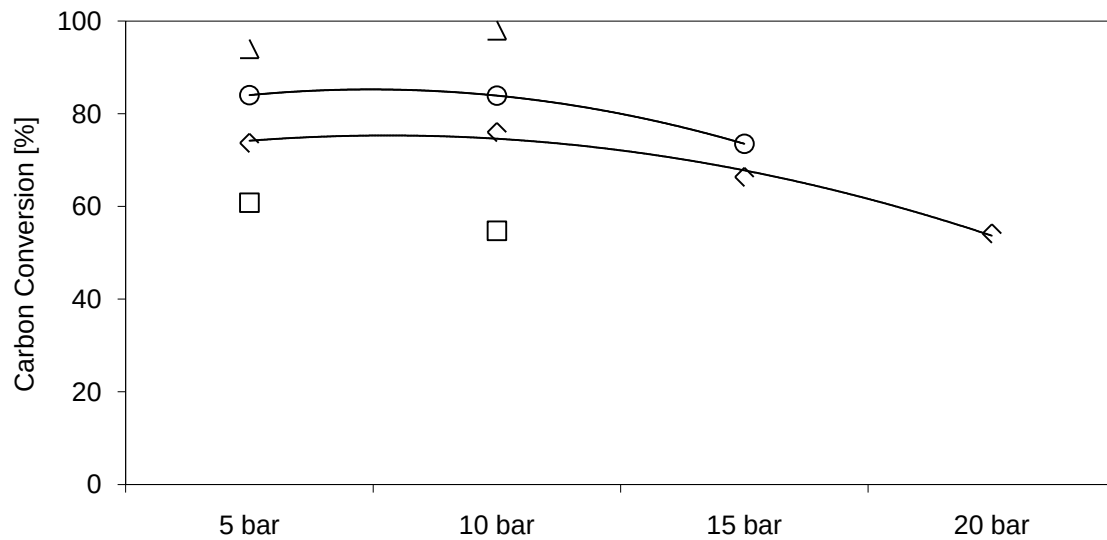


Figure 47: Oxy-fuel gasification of German Lignite at different conditions: Carbon conversion ($\square$ 850°C-CO₂, $\diamond$ 850°C -O₂/ CO₂, $\circ$ 850°C-steam/O₂/CO₂, Δ 950°C-O₂/CO₂)

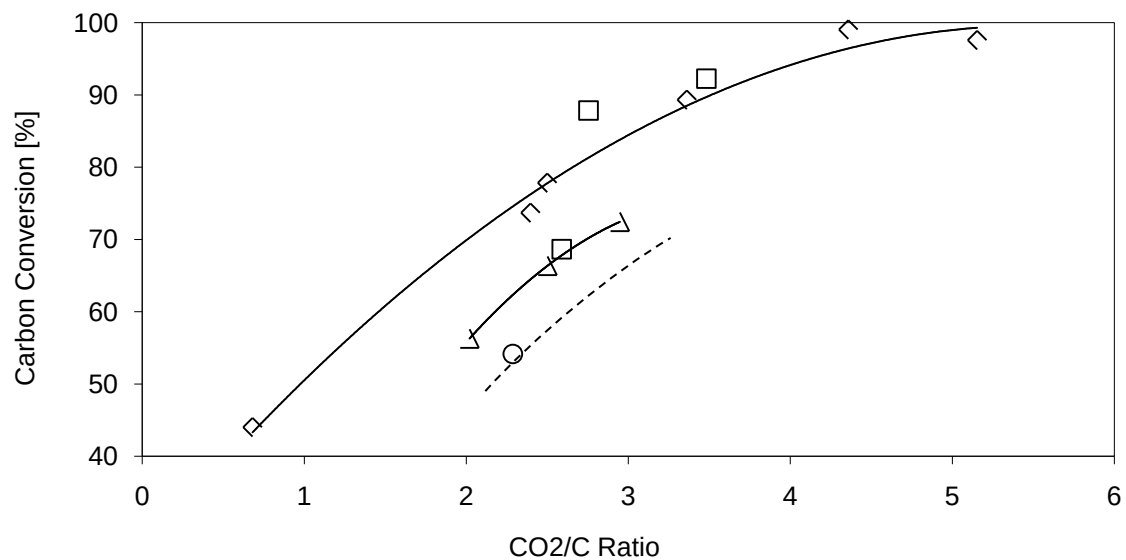


Figure 48: Oxy-fuel gasification of German Lignite at 850°C at different pressure and different CO₂/C ratios: Carbon conversion ($\diamond$ 5 bar, $\square$ 10 bar, Δ 15 bar, $\circ$ 20 bar)

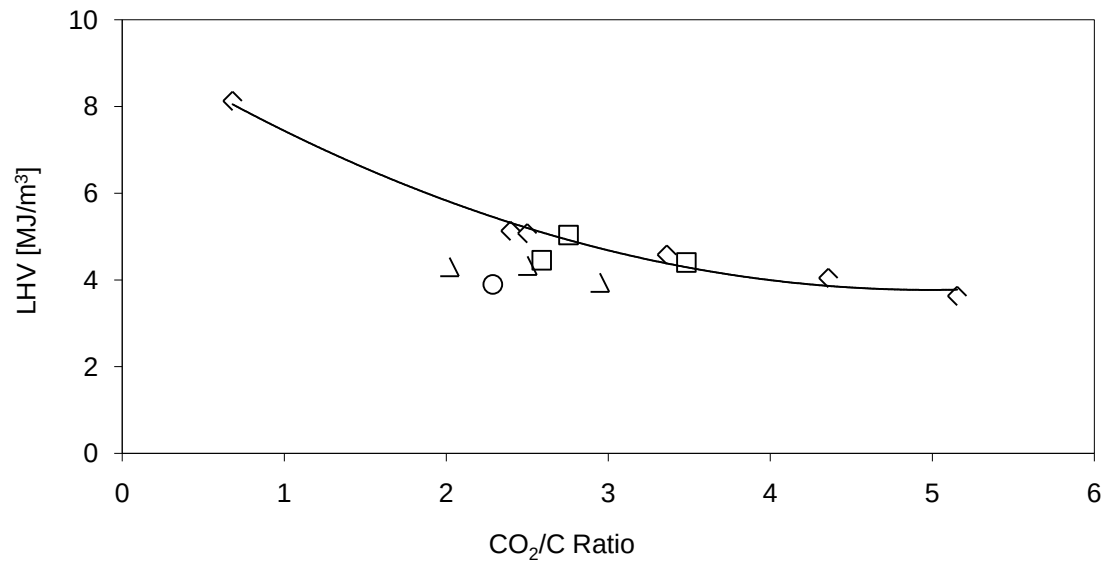


Figure 49: Oxy-fuel gasification of German Lignite at 850°C at different pressure and different CO₂/C ratios: Fuel gas Heating Value – LHV (◇ 5 bar, □ 10 bar, △ 15 bar, ○ 20 bar)

6.6 Summary

In this chapter the effect of pressure on the gasification performance was studied. Experiments in the FBR were carried out under a range of conditions including pyrolysis, CO₂ gasification, oxy-fuel gasification and steam addition. Chars recovered from the experiments were analysed using an optical microscope and an EM. Additional experiments were carried out using a high pressure WMR to produce data for comparison.

Decreasing carbon conversion with increasing pressure was the main effect identified with the FBR. Energy conversion and heating value of the fuel are decreasing as a consequence of this. This effect seemed to be especially significant above 10 bar. The results could not be explained based on decreasing volatile release as firstly the total amount of volatiles released decreased only by 3% (WMR finding) and secondly the extent of CO₂ gasification actually increased with increasing pressure in the WMR. From the optical analysis of the char particles it was found that the char surface at elevated pressure became increasingly covered with a reflecting layer. This is thought to be secondary char formed by thermally cracked tar, depositing on the primary char surface and is drastically reducing the char reactivity. The increasing fuel feeding rate and the subsequently higher particle density in the injection region of the FBR were identified as a main potential reason for the increased coverage of char particles with secondary char.

The methods to increase gasification performance established under atmospheric pressure were also used under elevated pressure. Decreasing char reactivity with increasing pressure required a higher reactivity gasification agent. This can either be achieved by increasing the temperature, adding steam or increasing the partial pressure of CO₂ in the system. The optimum method for an oxy-fuel process has to be chosen based on an overall process analysis.

7 Different Fuels and Fuel Mixtures

7.1 Introduction

Fluidised bed gasifiers are considered to be very fuel flexible. There are three main reasons for this: (1) The fuel does not have to be ground as fine as is required for entrained flow gasification. This is an important advantage for biomass and waste processing. (2) Operating temperature is below the ash softening point. Potential problems with corrosive ash are then avoided. (3) Change in fuel composition does not cause immediate problems, as the bed has high thermal capacity and mass and this dampens the effects of the variations. In general, fuels with high char reactivity are the preferred option as enhancing the conversion by increasing operating temperature is limited by the ash softening point. Therefore low rank coals, lignite and biomass are suitable feedstocks. Normally the processing of higher rank coals is only an option if the gasification process includes a combustion step for the remaining carbon in the ash or if the gasifier is operated under ash agglomerating conditions. A discussion of the available technologies is given in 2.3.1.3, page 32.

For the experimental work in this project a number of different fuels were available: a German lignite (GL), bituminous Polish coal (PC), bituminous Daw Mill coal (DM), Coalite and olive bagasse (OB). The analysis of the fuels is given in 3.3.3, page 89. Testing at the beginning of the project showed that all six fuel samples could be graded to the required particle size range and fed through the rotary valve. The bulk of the experimental work was carried out using lignite as it is the most suitable fuel for non-agglomerating fluidised bed gasification due to its high volatile content (2.3.1.3, page 32). A limited number of experiments were carried out with the other fuels in order to compare the operability of the gasifier and the gasification performance. The six different fuels were found to behave very differently upon injection into the gasifier. Therefore, the first part of the chapter reports on the operability of the gasifier with the different fuels and the implications the operability had on the experimental program and the reactor design. In the second part the gasification performance of the different coals are compared and in the third part the gasification performance of different lignite and olive bagasse mixtures is discussed.

7.2 Operability

The operability of the different fuels in the bench scale reactor was assessed according to two different criteria: (1) Injection into the bed, (2) In-bed agglomeration.

Injection into the bed: This was found to be the most critical part of the experimental set up. DM, PC and OB had the tendency to form agglomerates at the top of the spout and therefore block the line. No blockage occurred with GL under all conditions investigated. The blockage occurred within the first minutes after feeding was switched on. For DM this could be avoided by raising the bottom electrode. It was concluded that the agglomeration of fuel particles was related to the heating up of the particles while they were travelling through the spout line. Raising the bottom electrode moved the heated section of the reactor away from the spout line and therefore reduced the degree of gas/fuel preheating and the temperature at the injection point. For PC and OB this did not solve the problem. A number of additional measures were tried to avoid particle agglomeration and subsequent blockage: using different fluidising gas compositions (N_2 , O_2/N_2 , CO_2 , O_2/CO_2 and steam addition), increasing gas velocity from 0.15 – 0.4 m/s (at velocities > 0.3 m/s large quantities of bed material were entrained), operating with an empty bed and cooling the spout line with ice. However none of this allowed feeding for more than 5 min before the fuel agglomerated in the spout line, which prevented feeding. A final approach for PC was to pre oxidise the fuel²¹. After this treatment, no blockage of the spout and no agglomeration in the bed occurred. All experiments carried out with PC were done with the pre oxidised fuel. For OB it was found that it could be injected without problems if mixed with GL up to 50 wt%.

In-bed agglomeration: Two different types of agglomeration of particles in the bed were observed. (1) Ash-sand agglomeration for experiments at 950°C and high level of O_2 using GL (details discussed in 4.3.3.3, page 118). This agglomeration was only observed with GL (2) The small amount of PC that could be injected before the spout was blocked formed large agglomerates and caused the bed to de fluidise. This did not happen if pre oxidised fuel was used. Pre oxidising of the fuel significantly alters the fuel properties. In this case the reactive components on the outside of the fuel particles are probably reacting with the oxygen.

²¹ 60 g of fuel were placed in the reactor as initial bed material. The reactor was then heated to 200°C under air and held at temperature for 30 min before it was cooled down and the pre oxidised fuel could be recovered.

Therefore, upon injection the surface of the fuel particles is ‘inert’ and particles have a lower tendency to form agglomerates.

Summary: Initially it was thought that the agglomeration was related to the swelling number of the different fuels, but the analysis showed low values (0 – 0.5) for all fuels. In general it was concluded that the agglomeration of fuel particles in the spout line could be avoided by injecting ‘cold’ fuel into the bed, avoiding fuel preheating. However with the current set up this was not possible. In addition, fuel and gas are injected through the same line. A certain degree of gas preheating is desirable. Modification of the design of the current set up, which would allow cold fuel feeding are suggested and discussed in 11.2.1, page 224.

7.3 Gasification Performance – Lignite, Daw Mill and Polish Coal

7.3.1 Background

As mentioned above, suitable fuels for a fluidised bed gasifier are low rank coals with high char reactivity. In order to assess the differences in gasification performance between GL and higher rank coals, a number of experiments with DM and PC were carried out. For DM, the bottom electrode of the reactor was raised. Experiments with PC were carried out using pre oxidised fuel and pure CO₂ as gasification agent in order to avoid any temperature increase in the spout area by combustion. In addition, high gas velocities were used (0.28 m/s). Due to this limitation, no common basis for the comparison of all three fuels was possible. GL is compared separately with PC and DM. The discussion focuses on differences in the carbon conversions.

7.3.2 Discussion

GL and DM: Experiments were carried out at different temperatures and O/C ratios. The resulting carbon conversion is shown in Figure 50. It can be seen that the carbon conversion for DM (15 – 30%) is lower than for GL (60 – 80%). In both cases carbon conversion increases with temperature and O/C ratio, as expected. The exception is GL at 950°C where no increase in carbon conversion with O/C ratio occurs. This is related to the bed-ash agglomeration and is analysed in detail in 4.3.3.3, page 118.

GL and PC: Experiments were carried out with CO_2 and 25% steam/ CO_2 as gasification agent and at 850°C and 950°C . It can be seen from Figure 51 that carbon conversion increased with temperature and is higher for experiments with steam. Under this condition, 20% carbon conversion for PC and 80% for GL was achieved.

The results clearly show the difference in char reactivity of the lignite and the two higher rank coals. While for GL, high carbon conversion can be achieved at 850°C , for DM and PC significantly higher temperatures, in excess of 950°C and probably a higher reactivity gasification agent (steam) would be required to obtain acceptable conversion rates. In terms of temperature, the maximum temperature in a fluidised bed gasifier has to be well below the ash softening point (approx. 1200°C for PC and DM). Therefore, the maximum operating temperature would be around $1000 - 1100^\circ\text{C}$. The results show that oxy-fuel gasification requires low rank fuels, with a high char reactivity, not only because of the low operating temperatures in a fluidised bed reactor, but also because of the relatively slow char- CO_2 reaction rate. Replacing CO_2 completely or partially with steam would increase the gasification performance. However this would also reduce the efficiency of the plant as steam has to be produced at extra capital and operating costs.

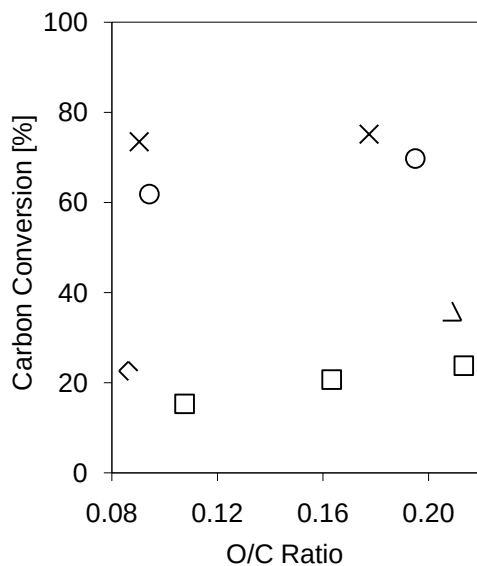


Figure 50: Oxy-fuel gasification of GL and DM – comparing carbon conversion ($u_s = 0.18$ m/s, raised electrode for DM) (○ GL 850°C , × GL 950°C , □ DM 850°C , ◇ DM 900°C , △ DM 950°C).

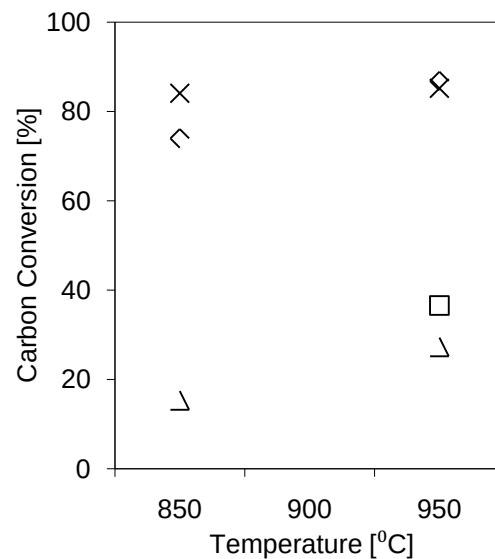


Figure 51: CO_2 gasification and steam/ CO_2 gasification of GL and PC – comparing carbon conversion ($u_s = 0.28$ m/s, pre oxidised PC) (× GL steam/ CO_2 , ◇ GL CO_2 , □ PC steam/ CO_2 , △ CO_2).

7.4 Co – Gasification of Olive Bagasse and Lignite

7.4.1 Background

The motivation to co-process OB and GL in this project came from two different directions: On the one hand co-processing of coal and biomass reduces the CO₂ emissions and is therefore a desirable process option. On the other hand OB could not be injected in the reactor on its own and had to be premixed with GL to enable it to be processed. The selection of the experimental conditions was guided by two limitations: (1) OB cannot be processed on its own and therefore possible synergetic effects of the co-processing cannot be identified. (2) The fuel feeding rate in terms of mass decreased with increasing percentage of OB in the fuel. This could not be compensated for by increasing the rotation of the rotary valve, as this was only possible in fixed steps.

Two different sets of experiments were carried out. In the first set, OB/GL was gasified with 10% O₂/CO₂ at 850°C. Fuel injection was only possible up to 20% of OB as at higher percentages the spout line blocked, due to the formation of agglomerates by OB (see above for details). Therefore, in the second set, pure CO₂ was used as the gasification agent to decrease the spout temperature and the gas velocity in the bed was increased from 0.18 to 0.29 m/s. Under these conditions mixtures with up to 50% OB could be processed. Care has to be taken when directly comparing results of sets 1 and 2. The gas velocity was increased by increasing the amount of CO₂ injected. Therefore, the CO₂/C ratio is higher in these runs, which affects the carbon conversion and dilutes the fuel gas with CO₂ (detailed discussion of increasing CO₂/C ratio in 4.4, page 121).

7.4.2 Discussion

7.4.2.1 Gasification Reaction and Carbon Conversion

The fuel gas composition, carbon conversion and the carbon feed rate of set 1 is shown in Figure 53 and the data of set 2 are shown in Figure 54. In both cases the carbon conversion increased with increasing amounts of OB in the fuel, while at the same time the carbon feed rate decreased. In set 2, 100% carbon conversion was achieved with fuel containing 30 or more percent of OB (this fuel composition could not be tested with the conditions in set 1 as explained above). To accurately assess the change in carbon conversion, two aspects have to be considered: (1) Increasing OB content in the fuel decreased the fuel feeding rate (carbon

feeding rate) and therefore the CO_2/C (and O/C rate for set 1) rate increased. (2) OB has a much higher volatile content than GL (67% compared to 44%) as determined by proximate analysis. Therefore it is reasonable to assume that OB is a more reactive fuel under these conditions and especially the reaction of CO_2 with OB char is faster than with GL char. Both factors contribute to the increasing carbon conversion. The higher char reactivity of OB could be shown by measuring the non-isothermal char combustion reactivity of the char recovered after the experiments (Figure 52). Clear differences can be seen between the chars produced by different OB/GL mixtures.

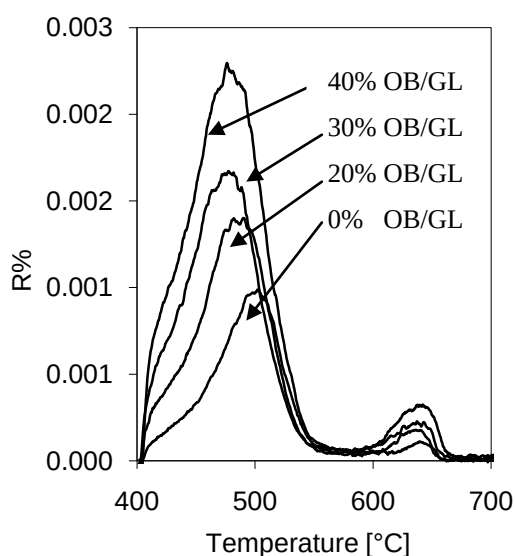


Figure 52: Non-isothermal char combustion reactivity of char recovered after experiments with different OB/GL mixtures.

It is important to clarify several points here to avoid confusion with previous conclusions: (1) Even if carbon conversion is complete, char from the start up phase remains in the bed and can be recovered. (2) Char recovered is a mixture of OB and GL char. The maximum in the reactivity curve is shifted to lower temperatures as the amount of OB char and therefore the reactivity increases. (3) Over the course of the project it was attempted to investigate the differences in combustion reactivity of GL char produced under different gasification conditions. This was found not to be possible, as the differences in char reactivity, as a result of the residence time distributions of chars from different experiments were similar to the differences caused by different gasification conditions. However, it was always possible to measure the difference between different fuels.

For cases with incomplete carbon conversion the amount of CO and CO₂ did not seem to be affected by the fuel composition. The reduction in carbon input was balanced by a higher carbon conversion and therefore the percentage of CO and CO₂ in the fuel gas was similar. However in the case of 100% carbon conversion (set 2, Figure 38, OB 30% or more percent in the feed mixture), the amount of CO in the fuel gas decreased with increasing OB in the fuel, simply because less solid carbon is fed into the reactor and therefore less CO₂ can react to form CO.

7.4.2.2 Hydrogen Product Distribution

The hydrogen product distribution of set 2 is shown in Figure 55. It can be seen that with increasing amount of OB in the fuel, less fuel-H is converted to H₂. The main reasons for that is probably the lower moisture content of OB compared to GL (3.7% compared to 13%) and the higher reactivity of OB-char. As a result the importance and extent of steam-char reaction and therefore the production of H₂ from steam decreases with increasing amounts of OB in the fuel. Interestingly the amount of hydrogen converted to CH₄ stays constant. This indicates that a similar fraction of fuel-hydrogen is released as CH₄ for both fuels during pyrolysis.

7.4.2.3 Conclusions

The results show that substitution of GL with OB can help to increase the carbon conversion without negatively affecting the gasification performance. For example when the gasifier is operated at 850°C with GL the carbon conversion is 75%. In order to increase the carbon conversion either the temperature or the CO₂/C ratio would have to be increased (alternatively steam could be added as well). All this would significantly reduce the efficiency of the gasifier. However replacing 30% of the fuel with OB would increase the carbon conversion, while maintaining the gasification efficiency. In addition it is a pathway to utilise waste for power generation and to reduce the CO₂ emission of the plant.

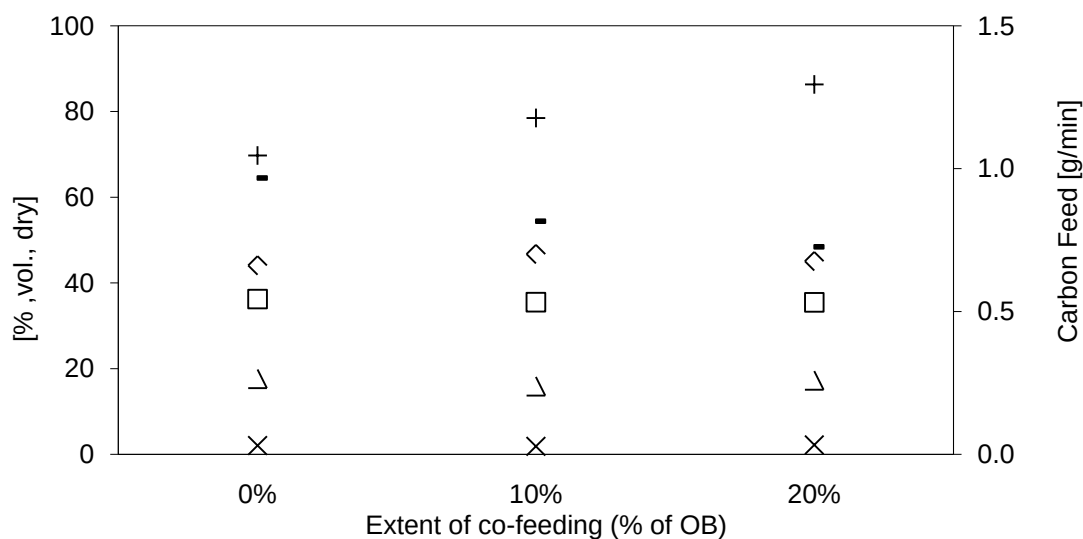


Figure 53: Set 1 - Co-gasification of OB and GL with 10%O₂/CO₂ at 850°C, 0.9 CO₂/C ratio – fuel gas composition, carbon conversion and carbon feed rate (□ CO₂, ◇ CO, Δ H₂, × CH₄, + Carbon Conversion [%], - Carbon Feed g/min).

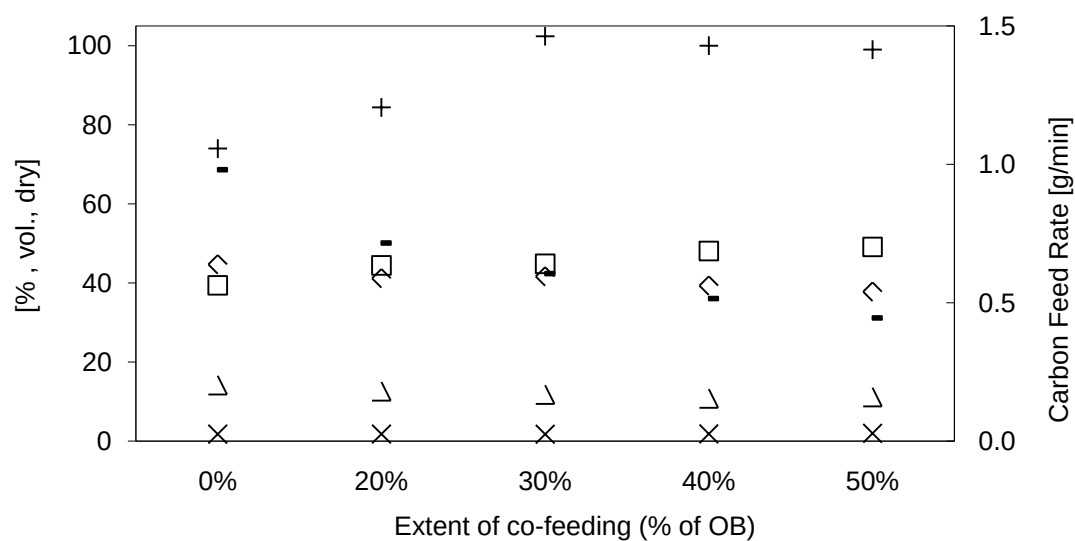


Figure 54: Set 2 - Co-gasification of OB and GL with CO₂ at 850°C, 1.4 CO₂/C ratio– fuel gas composition, carbon conversion and carbon feed rate (□ CO₂, ◇ CO, Δ H₂, × CH₄, + Carbon Conversion [%], - Carbon Feed g/min).

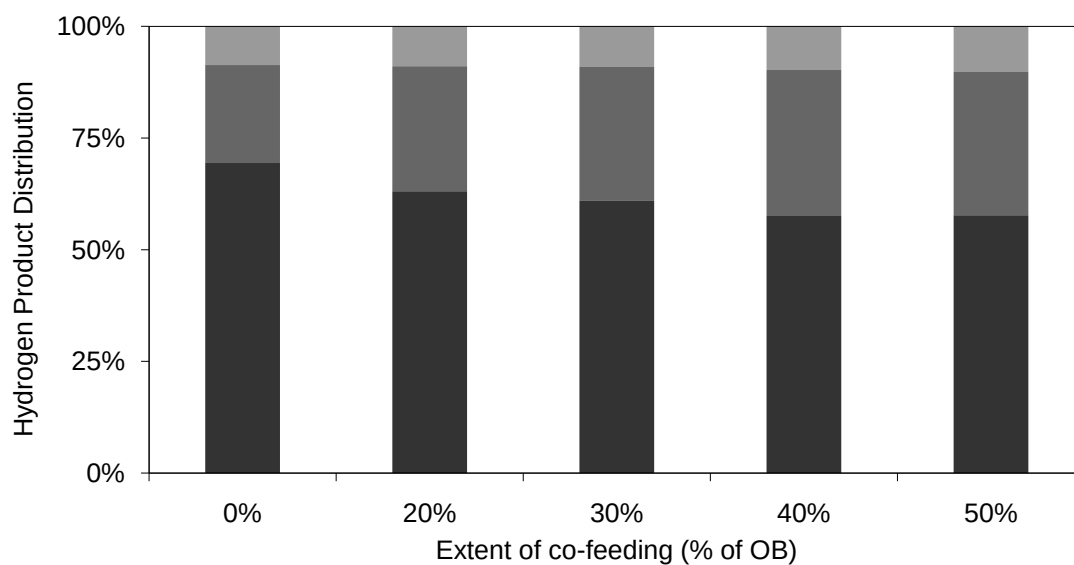


Figure 55: Gasification of OB/GL mixtures at different temperatures (set 2) – Hydrogen Product Distribution (■ H₂, ■ H₂O, ■ CH₄).

7.5 Summary

In this chapter the operability and gasification performance of three different coals and different OB/GL mixtures have been discussed. It was shown that all fuels tested (OB, DM and PC) apart from GL caused major operational problems. The fuel particles had a tendency to build agglomerates in the spout line and block it. The formation of agglomerates was related to the heating up of the particles before they were injected into the bed. In the case of DM raising the bottom electrode decreased the temperature in the spout enough to allow continuous injection of fuel. PC could only be injected if pre oxidised and OB had to be mixed with GL in order to be injected without problems. Mixtures with up to 50% of OB were possible by increasing the gas velocity and using pure CO₂ as gasification agent.

The gasification performance of the coals was compared based on the carbon conversion. Carbon conversions for DM and PC were around 20 - 30% compared to 60 - 80% for GL. This shows that GL is a suitable fuel for oxy-fuel gasification in fluidised bed, whereas DM and PC would have a poorer performance, which would mean their use would not be economic. Before a more detailed investigation with these fuels can be carried out, the carbon conversion needs to be raised to acceptable levels. Potential process modifications to achieve this would be, adding steam, increasing the temperature and using catalytic bed material. However, raising the temperature to this level requires raising extra heat by combustion in the reactor. This is not possible with the current set up as it would raise the spout temperature and prevent fuel feeding.

Co-processing of OB with GL proved to be a good way to improve the overall process performance. On the one hand carbon conversion can be increased by replacing part of the GL with OB while on the other hand the process efficiency is not affected. In addition processing biomass is a suitable way to produce energy from a waste feedstock and to reduce the carbon footprint of the process.

8 Emission of Pollutants

8.1 Introduction

Besides the major components of the fuel gas (CO , CO_2 , H_2 , CH_4), the gasification of solid fuels produces a number of minor compounds: solid particles, unconverted hydrocarbons, sulphur compounds, nitrogen compounds and trace elements. Depending on the downstream application, the fuel gas has to be cleaned to a certain degree before it can be further processed. If the fuel gas is combusted in a gas turbine on the one hand the requirements of the turbine in terms of gas quality have to be met, while on the other hand the emission targets after combustion have to be considered. In the case where the fuel gas is subsequently used for a chemical process, even stricter requirements on the purity of the gas stream are imposed mainly due to possible catalyst poisoning and the purity of the final product. Nowadays a number of well proven technologies are available to clean the fuel gas to any desired level. However gas cleaning processes are always associated with efficiency loss of the overall plant. It is therefore necessary to establish qualitative and quantitative trends for the emission of pollutants to firstly minimise pollutants by choosing appropriate operating conditions and secondly to establish the amount of pollutants to provide information for the selection and design for the gas cleaning system.

The chapter is divided into three parts. In the first part the emission of tar during the gasification process is investigated. The analysis of tar release in experimental reactors is heavily dependent on the set up and configuration of the experiment. Therefore, a detailed discussion of the related issues is given before the results are discussed. Part two discusses the release of H_2S during oxy-fuel gasification. It was chosen to analyse H_2S in the fuel gas because it is the major gaseous sulphur component under gasification conditions. Besides the trends in H_2S release with different operating conditions, a set of experiments is discussed investigating the possibility of S-retention using dolomite as bed material. The third part of the chapter analyses the different trends in the release of NH_3 in the fuel gas. Together with HCN , it is the major nitrogen component under reducing conditions and a major NO_x precursor if the fuel gas is combusted in a gas turbine.

8.2 Tar

8.2.1 Background

In terms of tar contamination of the fuel gas, fluidised bed gasifiers are between fixed bed gasifier and entrained flow gasifiers. While the high operating temperature in entrained flow gasifiers ensure a tar free product gas, significant amounts of tar are produced in an updraft fixed bed gasifier, as the fuel is slowly preheated by the syngas. In a fluidised bed gasifier the temperature is not as high as in an entrained flow gasifier, however a number of factors promote the cracking of tar. Any tar released by the fuel has to pass through the bed and then through the freeboard. This provides ample surfaces for tar cracking and increases the likelihood that large tar molecules will crack, partially to form gas. This is especially relevant if the gasifier is operated as spouted bed gasifier as it is the case in this study. In spouted beds fresh fuel is feed into the bed at the lowest possible position and therefore any tar released will have to pass the whole length of the bed before being entrained into the raw fuel gas stream. This configuration therefore ensures a large extent of tar cracking.

For this study, the raw fuel gas is cooled to room temperature immediately after it leaves the reactor in a tar trap kept between 0 and -10°C. Any carbonaceous material with a higher boiling point than room temperature is condensed and retained in the tar trap. After each experiment the total amount of tar condensed during an experiment is collected using solvents. The details of the tar collection procedure are giving in 3.2.1.3.3, page 85 . Two points are important for the discussion: (1) Tar collected after the experiment is the total amount of tar released during the duration of the run, including start up and steady state period. (2) Tar molecules can only be accounted for if they are condensed in the tar trap and if they are not lost during solvent evaporation.

The main purpose of the tar measurement was to obtain a better understanding of the processes leading to tar release into the fuel gas in a spouted bed gasifier. Therefore the first part of the discussion looks into the tar release during the different stages of an experiment. The aim is to find out if a constant amount of tar is released during the duration of the run or if the change in bed composition, more char and ash over time, affects the tar release into the raw gas stream. In the second part of the discussion, the influence of different gaseous atmospheres and temperatures on tar release is investigated. The third part of the discussion looks into tar release during co-gasification of OB/GL. Extensive tar formation and high tar

content of the fuel gas during fluidised bed gasification of biomass is one of the main issues of this technology. The investigation tries to establish to what extent increasing the amount of OB in the fuel increases the tar content of the raw fuel gas. In the final section of the discussion a number of collected tar samples are analysed using UV-F and SEC to compare the relative size of the tar molecules and the relative size of the aromatic chromophores in the tar.

8.2.2 Tar Deposition in the Reactor and Tar Release over Time

Different bed materials have different properties in terms of tar cracking. While silica sand is particularly inactive, char particles provide a very good surface for tar destruction [161]. As discussed in detail in chapter 5, page 136, the composition of the bed is changing over the duration of an experiment. In the beginning the bed consists mainly of silica sand while over time char and ash build up. To investigate if tar release is constant over time or if the changing bed properties are affecting tar release, three experiments were carried out under the same conditions (GL, 850°C, atmospheric pressure, 10% O₂/CO₂, constant fuel feeding rate of 1.7 g/min) but with different feeding time/total amount of fuel. After each experiment the condensed tar was collected. The results are shown in Figure 56. It can be seen that for all three experiments between 30 and 50 mg of tar were collected. This shows immediately that the tar release over time is not constant. Approximately the same amount of tar is collected after 10 min and after 45 min while the amount of fuel processed is 4.5 times higher. Taking into account the error in the tar collection (about +/- 10 mg) it can be concluded that the total amount of tar in each experiment is similar and produced during the first 10 min. After that no further tar is released into the fuel gas as it is presumably effectively cracked in the bed. This is probably an effect of char accumulation in the bed. As mentioned before, char provides a particularly good surface for tar cracking. In the beginning the bed mainly consists of sand, after 10 min approximately 2 - 5 g of char are in the bed and all the tar released by the fuel in the bottom of the bed is cracked.

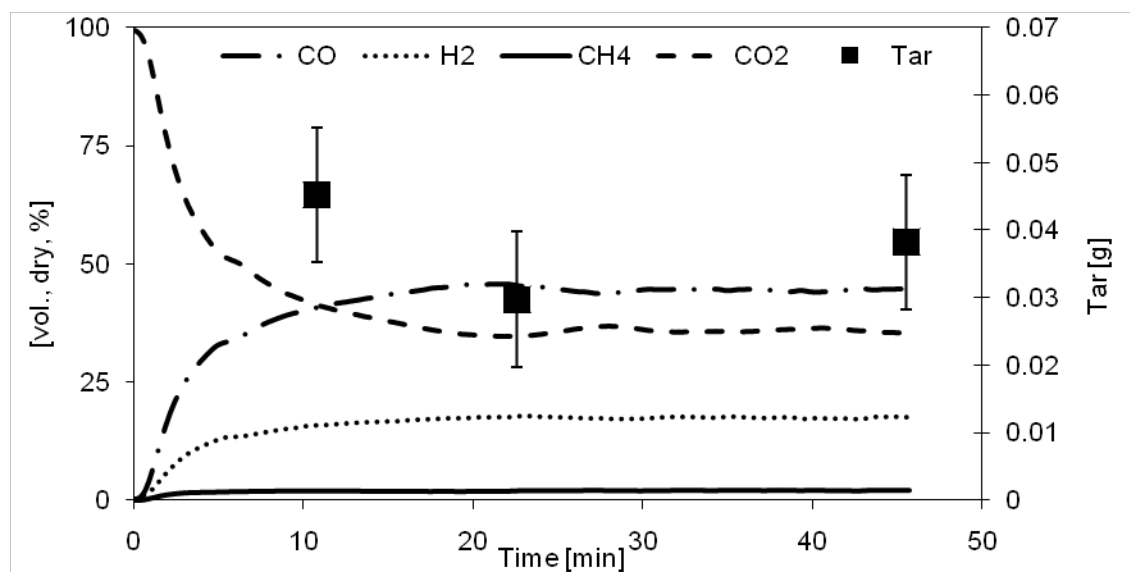


Figure 56: Total amount of tar collected after different times during oxy-fuel gasification of GL at 850°C and 10%O₂/CO₂.

8.2.3 Tar Released during Pyrolysis

Tar release under pyrolysis conditions was measured by collecting the total amount of tar after each experiment. In order to be able to compare the values, each experiment was carried out with the same amount of fuel and therefore lasted the same time. Figure 57 shows the amount of tar and the fuel gas composition. It can be seen that increasing the pyrolysis temperature decreases the amount of tar and increases the amount of gas. Tar molecules are cracked on contact with hot surfaces, like bed particles and the reactor wall, and break down to produce mainly CO and H₂ under these conditions. Therefore, the concentrations of H₂ and CO increase with increasing pyrolysis temperature. It is not possible to quantitatively correlate the change in tar release to the change in gas release as the bulk amount of tar during gasification is released during start up as discussed above. In 6.4.2, page 153, pyrolysis results under elevated pressure from the spouted bed reactor and a wire mesh reactor are compared. It can be seen that even under pyrolysis conditions tar is effectively destroyed in the bed under steady state conditions.

In comparison to tar release during gasification, under pyrolysis conditions the fluidising gas is not reacting with the volatile cloud. Especially if oxygen is present, large quantities of volatiles are combusted in the vicinity of the particle. This can be seen by comparing the amount of tar collected during a gasification experiment at 850°C (Figure 56, $m_{\text{tar}} = 0.03$ -

0.05g) and during a pyrolysis experiment (Figure 57, $m_{\text{tar}} = 1 - 1.5 \text{ g}$). In both cases tar is mainly released during start up and therefore is a function of the gaseous atmosphere.

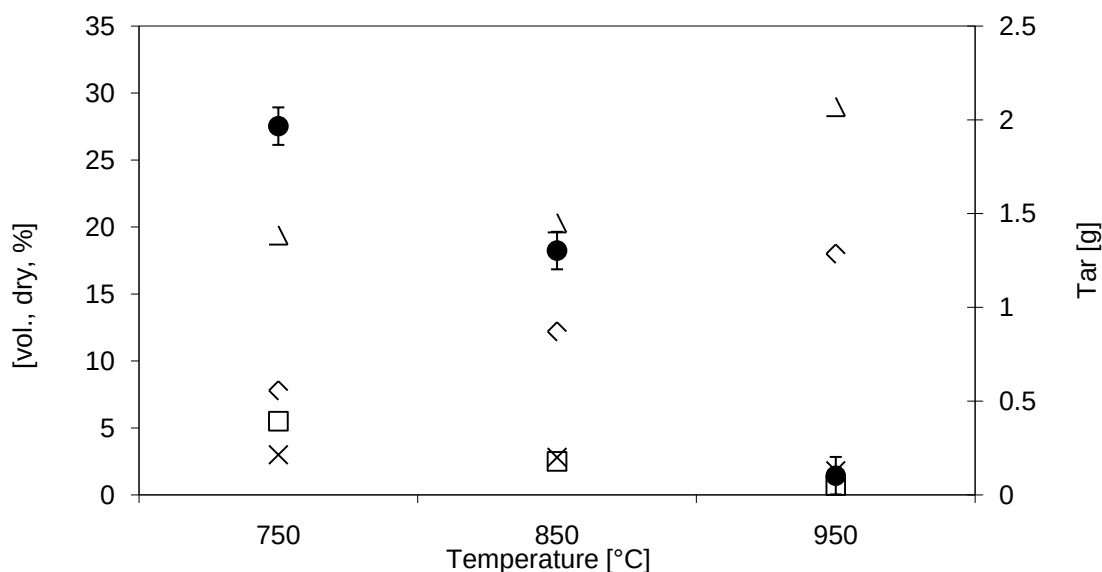


Figure 57: Tar released during pyrolysis of GL at different temperatures and under atmospheric pressure. ($\square$ CO, $\diamond$ CO₂, Δ H₂, $\times$ CH₄, $\bullet$ Tar)

8.2.4 Influence of Temperature and O/C Ratio

In order to investigate the influence of the gaseous atmosphere on the amount of tar released a suite of experiments was carried out. For each experiment, 10 g of DM coal were injected over a time of approximately 10 min into a preheated sand bed fluidised with different O₂/CO₂ mixtures. The amount of tar is presented as fraction of the initial fuel weight on a dry and ash free basis. Figure 58 summarises the results. Two main conclusions can be drawn: Firstly, increasing the amount of O₂ in the fluidising gas decreases the amount of tar. It decreases by approximately 2% if 10%O₂/CO₂ is used instead of 100% CO₂. Increasing the amount of O₂ increases the fraction of fuel combusted and causes high particle temperature - this increases the extent of tar cracking. In addition, O₂ could react with tar in the volatile cloud and therefore the final amount of tar would decrease. Secondly the amount of tar decreases with increasing gasification temperature. This is mainly due to the increased particle temperature in the bed and the equally increased wall temperature of the freeboard which promotes tar cracking. An additional factor could be the higher reactivity of the gas with increasing temperature. In the case of O₂ it can be assumed that under all conditions the reaction is complete and very fast. However, the reaction of carbonaceous material with steam, and especially with CO₂, is heavily dependent on temperature. More reactive volatile

material released by the fuel particles reacts with CO_2 /steam, decreasing the amount of tar produced.

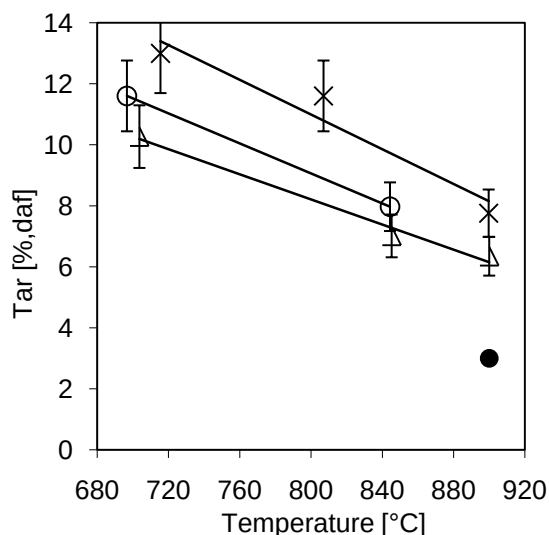


Figure 58: Tar released as percent of coal fed during oxy-fuel gasification of DM. (Δ 10 min-0.1 O/C, ○ 10 min-0.05 O/C, × 10 min-0.0 O/C, ● 30 min-0.05 O/C)

8.2.5 Tar Released during Co - Gasification

The possibility of co-processing OB and GL under oxy-fuel conditions has already been discussed in 7.4, page 169. One of the major problems in biomass gasification is the large amount of tar released from biomass into the raw fuel gas compared to coal gasification. Therefore the tar released during co-gasification was collected for a number of experiments. The change in tar release (tar per weight of fuel) is shown in Figure 59. The duration of each experiment was between 20 and 30 min. There seems to be an almost linear increase of tar release with increasing amount of OB in the fuel. It can be seen that increasing the amount of OB in the fuel from 20% to 50% doubles the amount of tar released. As discussed in 7.4.2.1, page 169, the carbon conversion under these conditions is complete. Especially with high percentages of OB in the fuel mixtures the produced char is very reactive and therefore the bed contains almost no carbon. This can further contribute to the increase in tar release as char content in the bed is a major promoter of tar cracking.

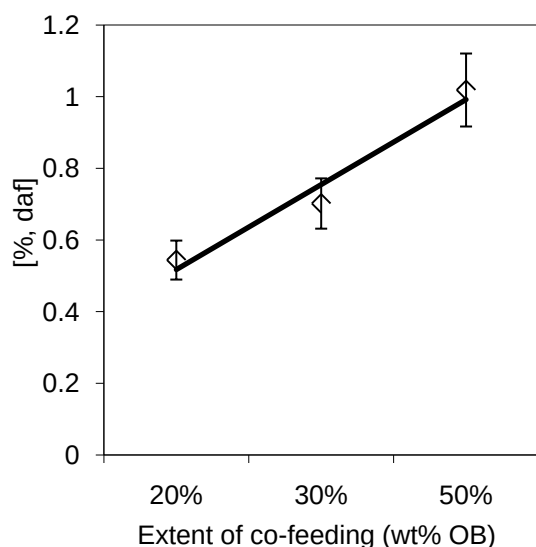


Figure 59: Tar released as % of fuel fed during oxy-fuel co-gasification of different mixtures of GL and olive bagasse.

8.2.6 Tar Analysis

A number of collected tar samples were analysed using SEC and UVF (for details of analytical method see 3.2, page 82). From this type of analysis information about the relative molecular size distribution and the size of aromatic chromophores of the tar molecules can be established. The analysis was carried out in order to investigate three points: (1) Differences between tars produced under different gasification temperatures, (2) comparing DM and GL tar and, (3) comparing tar produced from the gasification of different OB/GL mixtures.

Gasification temperature: The analysis of the tar from the tar trap by SEC (Figure 60, right) shows that tar collected from experiments at a higher gasification temperature has a longer elution time and therefore consists of smaller molecules than tar from experiments at a lower temperature. At higher temperatures, the large primary tar molecules break up to a greater extent than at lower temperatures, resulting in a higher concentration of smaller molecules. The UV-F analysis (Figure 60, left) of the tar does not show a clear trend.

Comparing DM and GL tar: UV-F analysis (Figure 60, left) confirmed that the tar produced from GL gasification consist of smaller molecules with smaller aromatic chromophores than DM tar. In addition DM tar seemed to be very corrosive. Steel parts of the reactor that were exposed to condensed tar showed corrosion damage. This is thought to be an effect of the higher sulphur content of DM compared to GL, resulting in tar containing more sulphur.

Comparing tar produced during co-gasification: UV-F analysis (Figure 61, left) of the tar collected after the co-gasification of different OB/GL mixtures shows that tar produced from mixtures with a higher fraction of OB contains smaller aromatic chromophores as the spectrum is shifted to lower wavelengths.

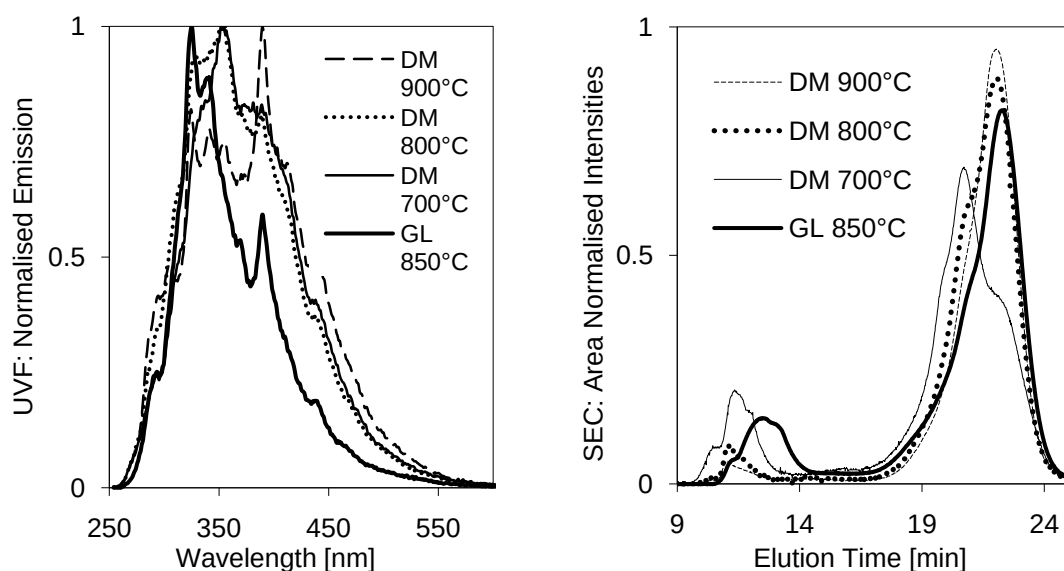


Figure 60: Left: UV-F emission spectrum of tar produced under oxy-fuel conditions (DM: 700°C, 800°C and 900°C; GL: 850°C). Right: Mixed-D column SEC chromatogram of tar produced under oxy-fuel conditions (DM: 700°C, 800°C and 900°C; GL: 850°C)

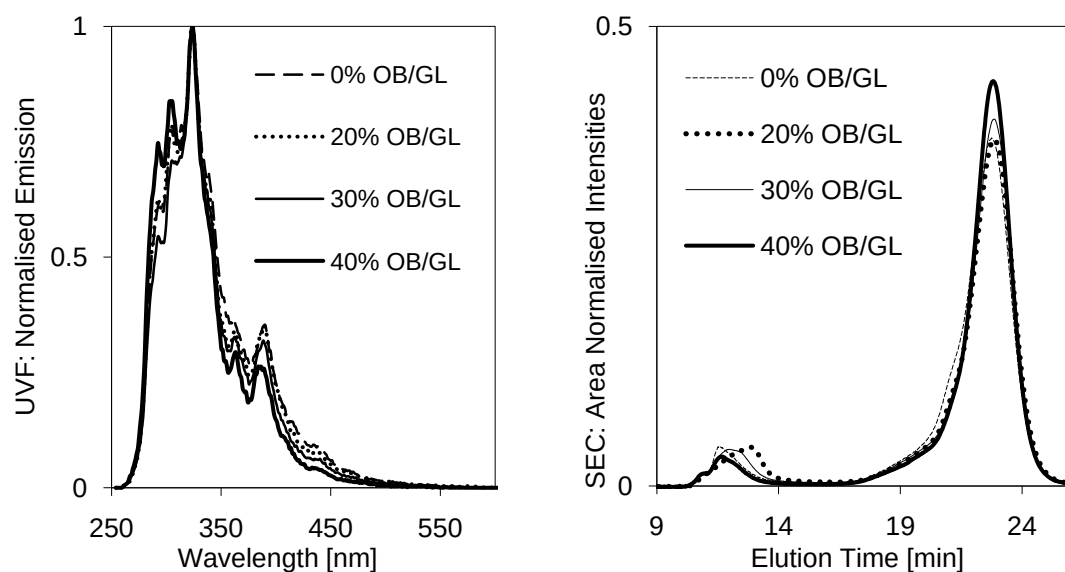


Figure 61: UV-F emission spectrum of tar produced under oxy-fuel conditions (different mixtures of OB and GL). Right: Mixed-D column SEC chromatogram of tar produced under oxy-fuel conditions (different mixtures of OB and GL)

8.2.7 Conclusions

The main findings of this section can be summarised in four points: (1) The tar collected after each experiment was mainly produced during start up. After the bed contained 2 -5 g of char, all the tar was cracked. (2) Increasing temperature increased the extent of tar cracking as the particle temperature in the bed and the wall temperature of the freeboard increased. Both contribute to the increase in tar cracking. (3) Increasing the partial pressure of O_2 in the fluidising gas decreased the amount of tar. (4) Increasing the amount of biomass (OB) in the fuel mixture linearly increased the amount of tar.

8.3 Hydrogen Sulphide

8.3.1 Background

As mentioned in the introduction to this chapter, the main gaseous sulphur species under reducing conditions in a gasifier is H_2S . Therefore the discussion of the experimental results focuses on the H_2S concentration in the fuel gas and the sulphur released as H_2S is used as an overall indicator to judge how much sulphur is retained and how much is released. The chemical and physical mechanisms related to the sulphur release and the sulphur capture in fluidised bed gasification are reported in 2.4.7.3, page 62 and are used as background information for this discussion. Here the specific experimental conditions used in this study and their influence on the H_2S concentration in the fuel gas are discussed in more detail.

The discussion of the experimental results is structured into four sections. The first part deals with the influence of temperature and gasification agent on the concentration of H_2S in the fuel gas. The second part focuses on the effect of pressure on the release of H_2S . In the third part, the differences in sulphur release from different fuels are discussed. The last section explores the possibility to increase the sulphur capture by adding dolomite to the bed.

The concentration of H_2S in fuel gas was measured directly (method of H_2S measurement in 3.2.1.3.2, page 84) and gives an indication about the amount of sulphur released during the process. In addition it can be used to judge if and what type of gas cleaning would be required if the process was scaled up. However further information about the carbon conversion and the total amount of sulphur in the fuel is required to judge the effect of operating conditions on sulphur release/retention. Large differences in carbon conversion can have a significant impact on the amount of sulphur released as sulphur might be still embedded in the carbon matrix. It has to be noted that the sulphur release is by no means strictly related to the carbon conversion. Presenting the data in this form simply helps to see the data in a broader context. Therefore, in the first three sections, the experimental results are presented as: (1) concentration of H_2S in the fuel gas, (2) fraction of total sulphur in the fuel released as H_2S and, (3) fraction of total sulphur in the fuel released as H_2S divided by the carbon conversion. In this way a more complete assessment of the results is possible and a number of additional conclusions can be made.

8.3.2 Effect of Gasification Agent and Temperature

The results are summarised in

Figure 62. The experimental data allow the influence of temperature and gasification agent to be discussed. In the temperature range from 750°C to 950°C O₂/N₂, CO₂ and steam/CO₂ were used. Therefore, the influence of a high partial pressure of CO₂, steam and temperature can be assessed.

Steam addition: Gasification with steam addition produces a fuel gas with a higher concentration of H₂S than CO₂ or O₂/N₂ gasification. Steam and H₂ are known to promote sulphur gasification and to decrease the sulphur capture by inorganic material. Furthermore, steam and H₂ increase the H₂S/COS ratio. This leads to higher concentrations of H₂S in the fuel gas with increasing steam input. There seems to be an upper limit to the effect as between 25% and 50% steam addition does not seem to have a major effect anymore. As an example of this effect and to confirm it is not an effect of carbon conversion/fuel gas flow rate, the results at 950°C can be used. At 950°C carbon conversion is complete for CO₂ and for steam/CO₂ gasification (4.6, page 133). The data show that for CO₂, the fuel gas contains 300 vpm H₂S and 30% of sulphur in the fuel is released as H₂S, while for 25% and 50% steam/CO₂ the fuel gas contains 500 vpm H₂S and 40% of sulphur is released as H₂S.

High partial pressure of CO₂: The partial oxidation with O₂/N₂ leads to a lower concentration of H₂S in the fuel gas than the gasification with CO₂. For these experimental conditions the differences in carbon conversion are large. Therefore, the sulphur release is corrected for the carbon conversion. It can be seen that at 850°C the sulphur released as H₂S is 30% for both cases, while at 950°C, significantly more sulphur is retained in the O₂/N₂ case. Assuming the Ca in the lignite ash (Table 16) as the main inorganic compound to capture S, an increased partial pressure of CO₂ would decrease the calcination reaction and therefore decrease the extent of the fast, indirect sulfidation²². The use of O₂ suggests that part of the sulphur can be converted to SO_x. However, as discussed in 2.4.7.3, page 62, the concentration of SO_x compared to H₂S is normally small. Furthermore, SO_x would be formed in the spout region and is likely to be converted to H₂S while passing through the bed.

²² Indirect sulfidation: Calcination of CaCO₃ and subsequent reaction of CaO with H₂S to CaS. Details discussed in 2.4.7.3, page 59.

Temperature: The concentration of H_2S in the fuel gas is constant for CO_2 gasification, decreases slightly for steam/ CO_2 gasification and decreases sharply for O_2/N_2 gasification, with increasing temperature. These effects can be explained with the background information discussed in 2.4.7.3, page 62. Increasing temperature on the one hand enhances the break up of organic sulphur structures and therefore the amount of S in the gas phase is increasing. On the other hand, increasing temperature promotes sulphur-ash reaction, leading to an increased amount of sulphur being retained in the solid material. These two competing effects result in the temperature dependency seen here. Different gaseous atmospheres have different effects on the retention and release of sulphur causing different behaviours with increasing temperature. An example is the comparison between CO_2 and O_2/N_2 discussed above. In the case of 25% steam/ CO_2 it can be seen that 100% sulphur (relative to the carbon conversion²³) is released at 750°C. The value decreased to 50% for 850°C and 950°C, showing the increased extent of sulphur retention by inorganic material (high content of Ca – see Table 16) with increasing temperature.

²³ The fuel-S to gas conversion is the same as the fuel-C to gas conversion

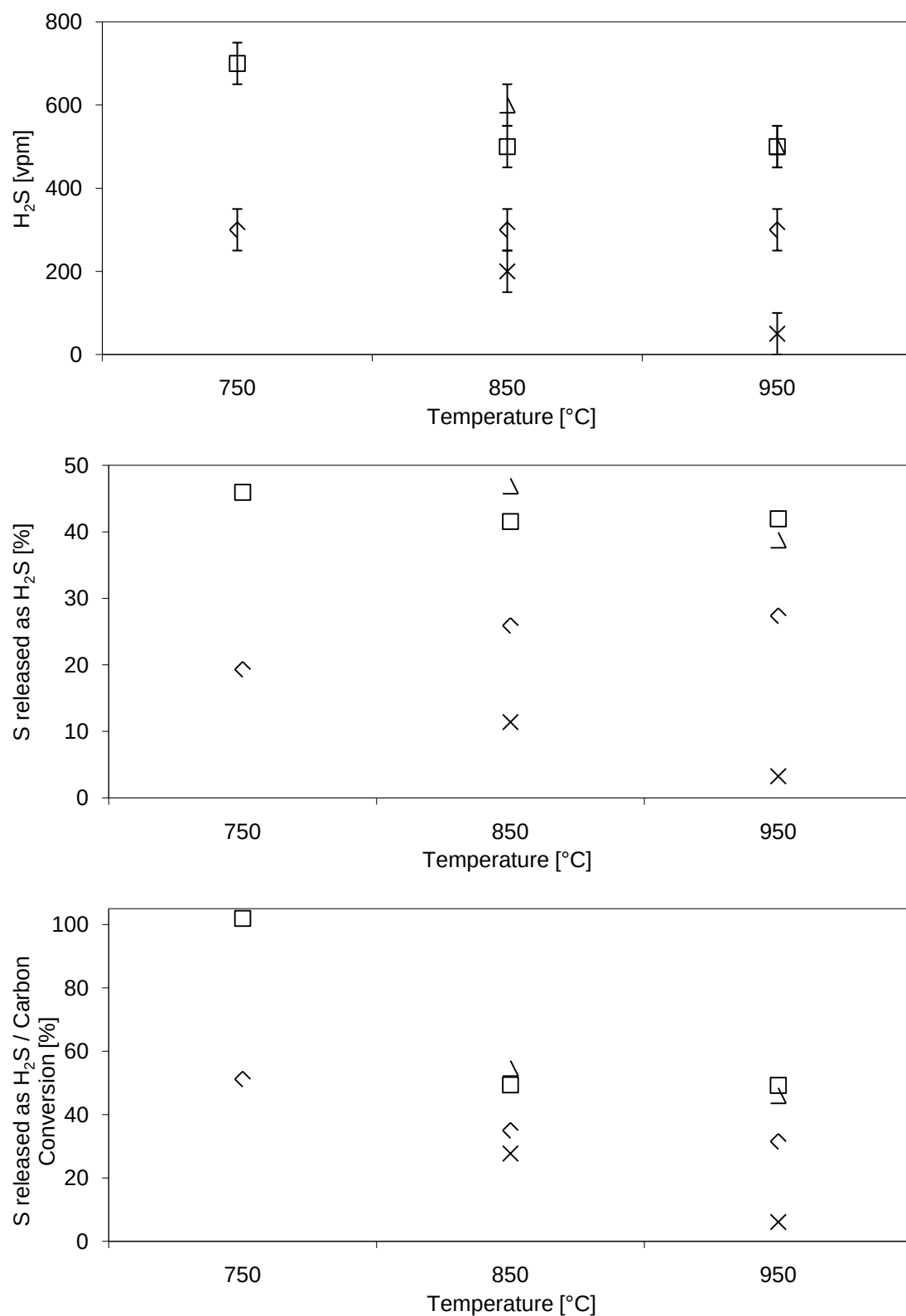


Figure 62: H₂S in the fuel gas. Effect of gasification temperature and gasification agent. Top: concentration in the fuel gas, Middle: Percentage of sulphur in the fuel released as H₂S. Bottom Percentage of sulphur releases as H₂S corrected for carbon conversion. (◇100% CO₂, □ 25% Steam/CO₂, Δ 50% Steam/CO₂, × 100% N₂)

8.3.3 Effect of Pressure

The results are summarised in Figure 64. In the pressure range from 1 to 15 bar, fuel was gasified with O_2/CO_2 and with O_2 /steam/ CO_2 at $850^\circ C$ and with O_2/CO_2 at $950^\circ C$. Therefore the influence of increasing pressure under different gasification conditions (steam addition and higher temperature) can be discussed.

Overall effect of pressure: It can be seen that the concentration of H_2S in the fuel gas increases with pressure for all conditions investigated. This trend is confirmed by analysing the release of total sulphur as H_2S and after correcting for carbon conversion. At 15 bar the fuel gas contains between 100 and 200 vpm more H_2S than at atmospheric pressure. This corresponds to a 30% increase in the release of total sulphur as H_2S . At $850^\circ C$, 15 bar and a steam/ O_2/CO_2 atmosphere almost 80% of the total sulphur (100% if corrected for carbon conversion) is released as H_2S . This shows to what extent an increase in pressure inhibits the sulphur retention by the inorganic coal components. An indication of the underlying effect can be obtained by calculating the equilibrium concentration of H_2S at different pressures for the direct and indirect sulfidation of Ca. The equilibrium is calculated using the equation and data given in Appendix D.2, page 249. The equilibrium calculation in Figure 63 shows an increase of the maximum H_2S concentration from 100 (10) to 1800 (150) vpm for the direct (indirect) with increasing pressure. This shows to what extent increasing pressure can lead to an increasing H_2S concentration.

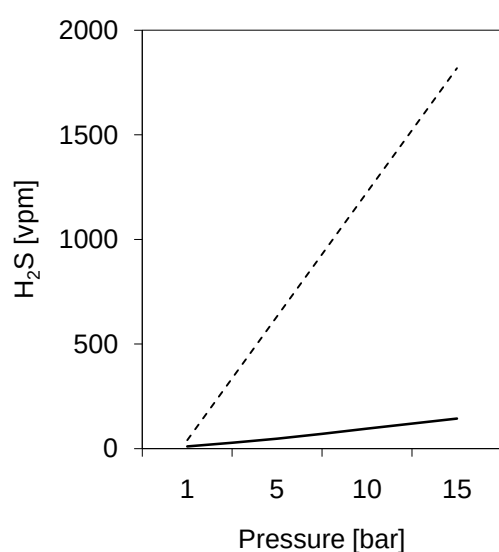


Figure 63: Equilibrium concentration of H_2S for direct sulfidation (dashed line) and indirect sulfidation (solid line). Values calculated based on H_2O and CO_2 concentration in the fuel gas for O_2/CO_2 gasification at $850^\circ C$ of GL. Calculation given in Appendix D.2, page 249.

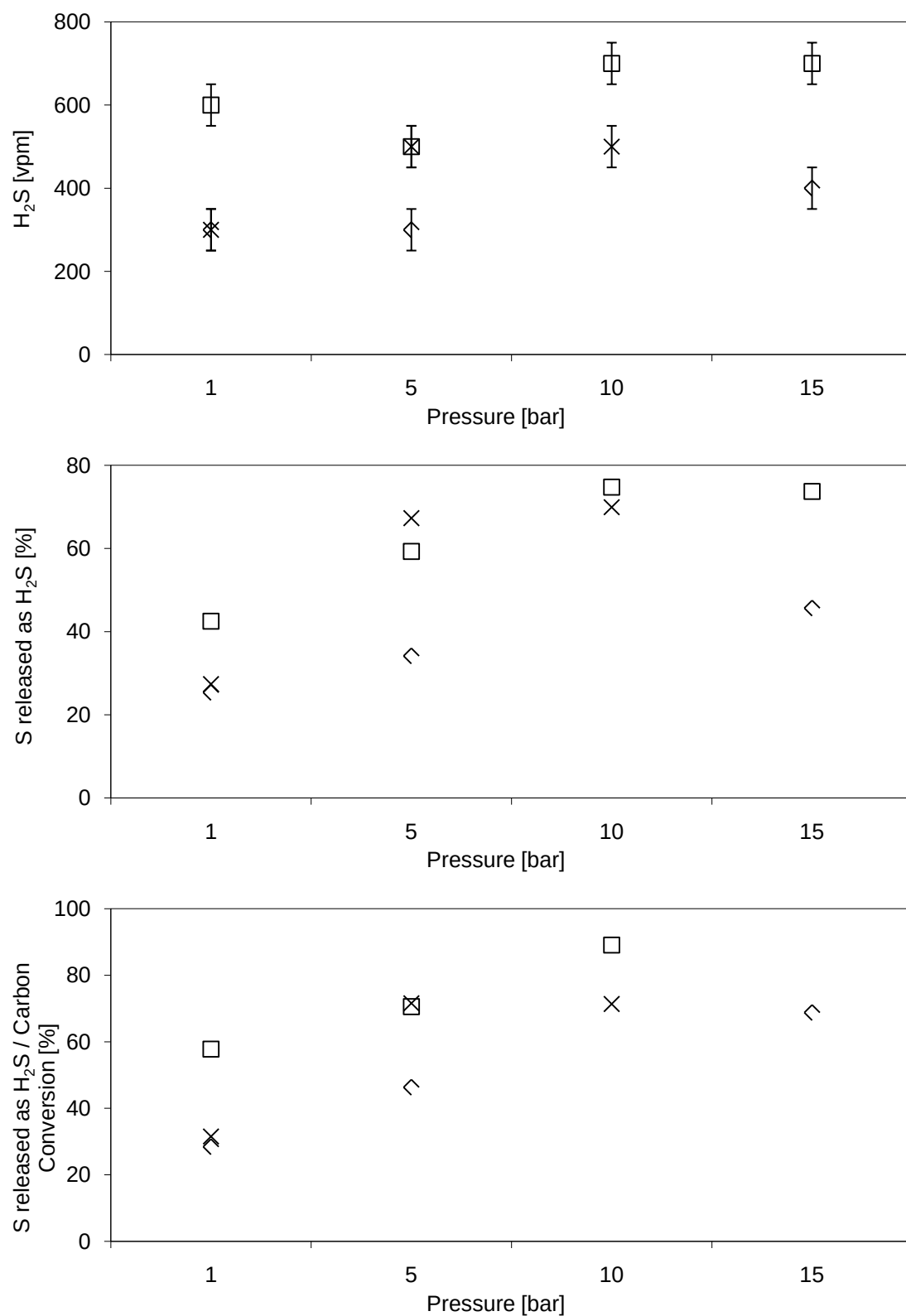


Figure 64: H₂S in the fuel gas. Effect of Pressure. Top: concentration in the fuel gas, Middle: Percentage of sulphur released as H₂S. Bottom Percentage of sulphur released as H₂S corrected for carbon conversion. (◇ 10% O₂/CO₂-850°C, □ Steam/O₂/CO₂-850°C, × 10% O₂/CO₂-950°C)

8.3.4 Effect of Different Fuels

In order to investigate the sulphur release from different fuels, 3 types of coal and different mixtures of GL and OB were gasified and the H_2S concentration in the fuel gas measured. The sulphur content and the Ca content of the 4 different fuels investigated in this study are shown in Table 16. It can be seen that with the exception of DM, all other fuels contain between 3-4 times more Ca than S and therefore a certain degree of sulphur capture as CaS can be expected even for experiments without added dolomite or limestone. It can be seen that for mixtures of OB and GL (20 - 50% OB/GL), the sulphur content of the fuel decreases while the Ca/S ratio increases

Table 16: Ca and S content of the different fuels (weight percent/as received.)

	Ca [%]	S [%]	Ca/S
GL	2.0	0.23	8.8
DM	0.6	1.61	0.40
PC	1.5	0.41	3.6
OB	0.93	0.06	15

The results are summarised in Figure 65. The concentration of H_2S in the fuel gas is broadly linearly related to the sulphur content of the fuel. For the fuels with less than 0.5% sulphur content a H_2S concentration of <500 vpm was measured while for DM with a sulphur content > 1.5%, between 1500-2000 vpm was detected. Despite the very large differences in Ca content and Ca/S ratio of the different fuels, the dominating factor seems to be sulphur content. However the carbon conversions were different. While for GL and OB/GL mixtures, the carbon conversion is complete or near complete, for PC and DM only a maximum of 40% (detail see 7.3, page 167) of the carbon was converted to gas. Taking this into account and correcting the data for the actual carbon conversion it can be seen that for all three coals the ranges of sulphur released as H_2S are undistinguishable (30 - 50%). This gives an indication that in case of PC and DM sulphur is retained in the un-converted carbon matrix. In case of similar carbon conversion for all fuels that would again mean a linear relationship between sulphur content and H_2S in the fuel gas. In the case of OB/GL mixtures the sulphur release as H_2S is significantly less than for pure GL and smaller than expected from its sulphur content. It seems that for mixtures in general a larger degree of sulphur is retained or a larger fraction of sulphur from OB is released as compounds other than H_2S .

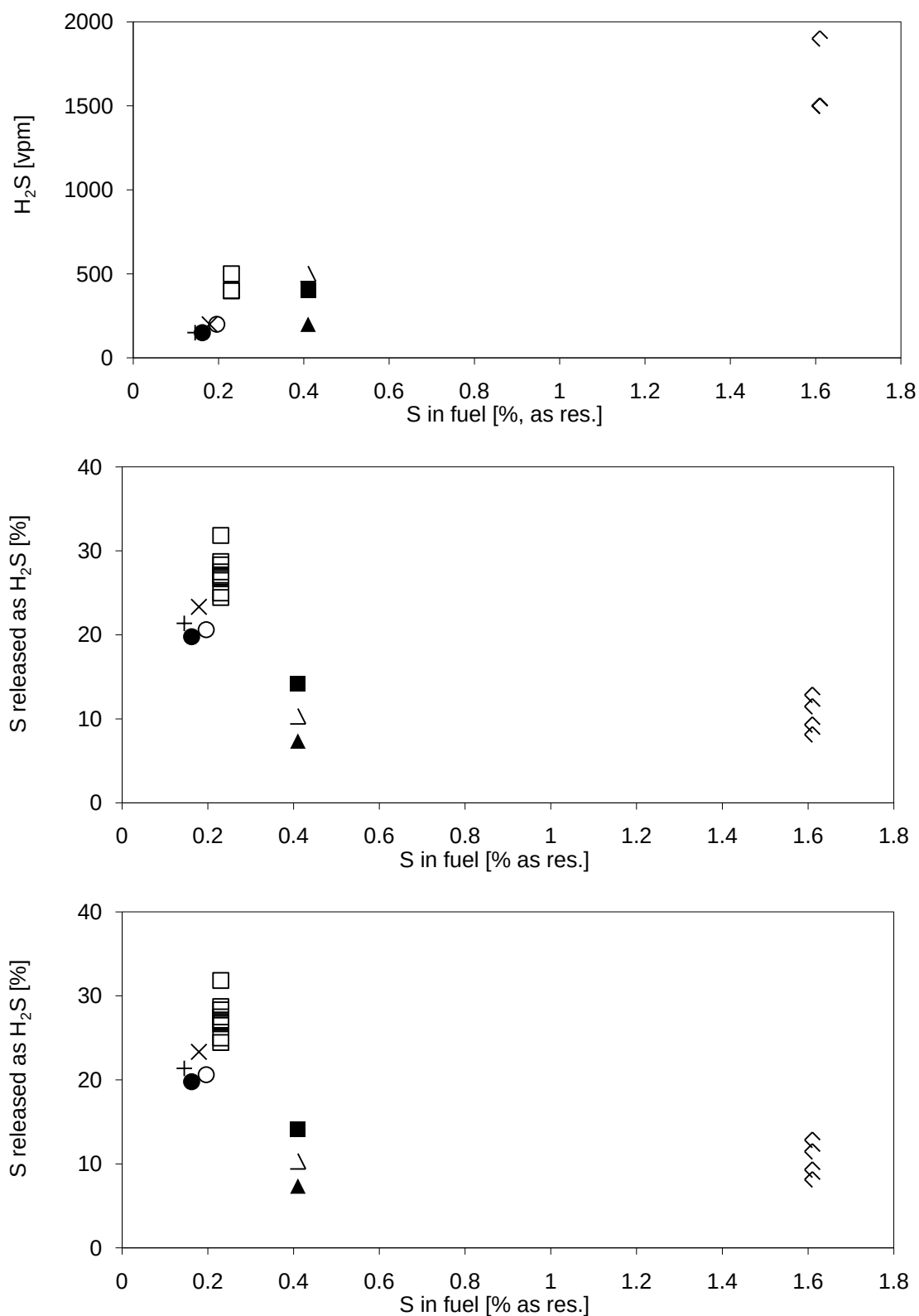


Figure 65: H₂S in the fuel gas. Effect of Fuel. Top: concentration in the fuel gas, Middle: Percentage of sulphur releases as H₂S. Bottom Percentage of sulphur releases as H₂S corrected for carbon conversion. (all experiments at atmospheric pressure - ◇ Daw Mill Coal (10%O₂/CO₂, 850°C, different fuel feeding rate), □ German Lignite (10%O₂/CO₂, 850°C), Δ Polish Coal (100%CO₂, 850°C), ▲ Polish Coal (100%CO₂, 950°C), ■ Δ Polish Coal (steam/CO₂, 950°C), OB/GL Mixture (○ 20% OB, x 30% OB, ● 40% OB, + 50% OB - 100% CO₂, 850°C))

8.3.5 Retaining Sulphur in the Bed

Introduction: A main feature of a fluidised bed gasifier is its capability to retain a large amount of sulphur released in the bed by using additional bed material, like dolomite or limestone. The sulphur capture is based on the formation of CaS which is then removed from the bed with the ash. As mentioned before, there are two ways CaS is formed: (1) Direct formation from CaCO_3 and H_2S (slow and endothermic reaction). (2) Indirect sulfidation: CaO with H_2S forms CaS (fast and exothermic). For the indirect way, the CaCO_3 needs to be calcined first. The equilibrium constant of the calcination reaction depends on the partial pressure of CO_2 in the system. For an oxy-fuel blown gasification process this means a higher temperature is needed for the calcination (Figure 66). As discussed in 2.4.7.3, page 62, the optimum temperature for the sulphur capture is at the calcination temperature. At this point the equilibrium concentration of H_2S of the indirect- and direct sulfidation is at a minimum as shown in Figure 67.

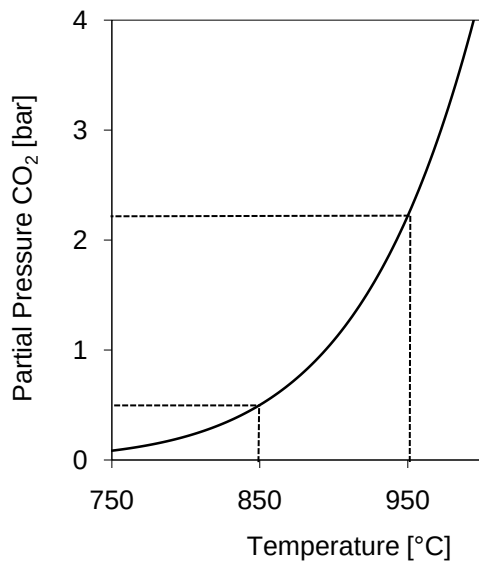


Figure 66: Calcination temperature of CaCO_3 : Equilibrium partial pressure of CO_2 at different temperatures.

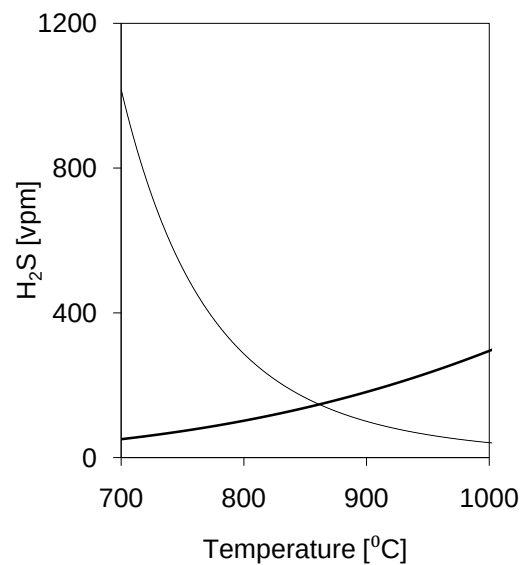


Figure 67: Equilibrium concentration of H_2S for the indirect (solid line) and direct (dashed line) sulfidation. Data calculated for 60% CO_2 and 20% H_2O and 1 bar. Calculation given in Appendix D.2, page 249.

Discussion: A set of experiments was carried out to investigate the effect of dolomite in the bed on the H_2S concentration in the fuel gas. The results are summarised in Figure 68. The effect of dolomite on the gasification performances is discussed separately in 5.3, page 142. The first set of experiments was carried out at 850°C with GL under atmospheric pressure using 10% O_2/CO_2 as gasification agent. For one experiment 3% of the fuel was replaced by dolomite. This did not lead to a reduction of the H_2S concentration in the fuel gas. The most likely reason is that the concentration of dolomite in the bed during the duration of the experiment was too low. A total amount of 1 g built up in the bed during the test, compared to 60 g of sand used as initial bed material. In a following set of experiments, the 20, 40 and 60% of sand as initial bed material were replaced by dolomite. In this way the total amount of dolomite was increased to 12, 24 and 36 g. As the results show, this increased the sulphur retention and the H_2S concentration in the fuel gas decreased from 300 to 200 vpm. The last experiment was carried out at 950°C with 60% of dolomite, under otherwise comparable conditions and the H_2S concentration decreased to 50 vpm. In terms of total sulphur this means 96% of the fuel sulphur was retained. As mentioned above, the calcination temperature increases with increasing partial pressure of CO_2 . The experimental data indicate that at 850°C the sulphur retention is mainly through direct sulfation, while at 950°C the temperature is high enough to calcine CaCO_3 and the fast route of indirect sulfation becomes favoured.

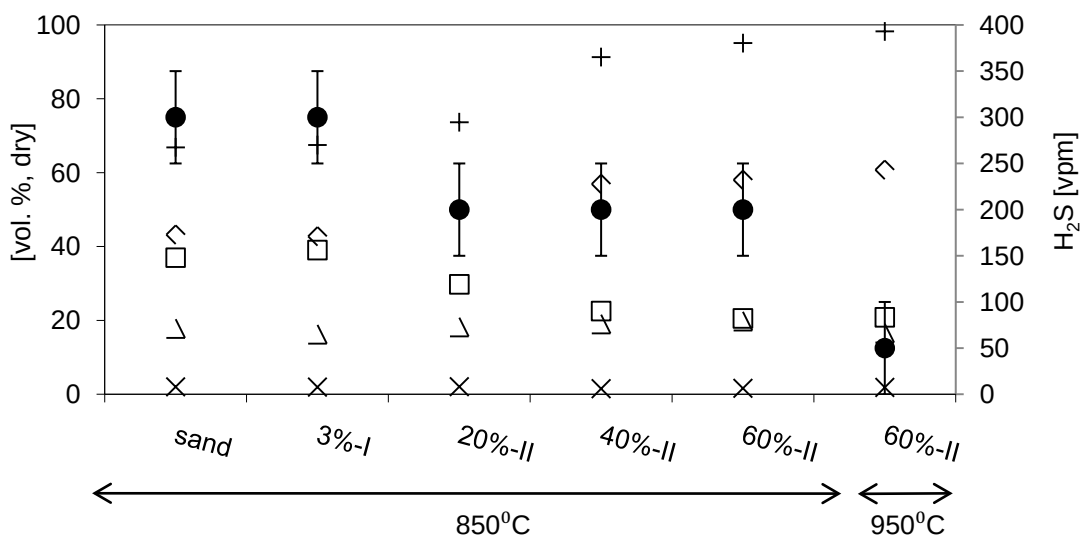


Figure 68: Oxy-fuel gasification of German lignite with different dolomite/sand mixtures as initial bed. (I: co-feeding with the fuel, II: mixed with initial bed material, $\square$ CO_2 , $\diamond$ CO , Δ H_2 , $\times$ CH_4 , + Carbon Conversion [%], $\bullet$ H_2S)

8.3.6 Conclusions

The extent to which sulphur is retained or released with increasing temperature depends on the fuel and the operating conditions. Increasing the partial pressure of CO_2 , steam, and increasing overall pressure increases the amount of sulphur released. Adding dolomite to the bed reduces the sulphur content of the fuel gas. However due to the high partial pressure of CO_2 in oxy-fuel gasification, higher temperatures, 950°C in this case, are required to ensure calcination of CaCO_3 . A maximum of 94% of sulphur could be retained in the bed.

The amount of sulphur released is directly linked to the amount of sulphur in the fuel. However it seems that mixing OB and GL has a beneficial effect on the overall sulphur retention as less sulphur is released than would be expected from the sulphur content of the fuel mixture.

8.4 Ammonia

8.4.1 Background

In order to discuss the results it is necessary to review two points: the characteristics of the NH_3 collection and analysis and the evaluation of the measured data. In this study, the NH_3 release during gasification was measured by analysing the condensed water in the tar trap and the water from the bubbler for its NH_3 content. Due to its very high water solubility all the NH_3 is stripped from the gas stream. However during this process the total amount of NH_3 released during the whole process – start up and steady state – was collected and only an approximation of the NH_3 release per unit fuel gas (mass of fuel) could be obtained. The main uncertainty is the assumption that the NH_3 release is constant over the duration of the whole experiment. Nevertheless clear trends in the amount of NH_3 release could be obtained from the experimental data. The second point that needs to be reviewed is the information content of the results. The H_2S measurement discussed before could be used to judge the overall sulphur release from the fuel, as under reducing conditions the major fraction of sulphur is released as H_2S . This, however, is not the case for NH_3 and the release of fuel nitrogen. As discussed in 2.4.7.2, page 59, part of the nitrogen is also released as HCN , N_2 and NO_x whereby the fraction of HCN and N_2 can be comparable to the amount of NH_3 . Based on this constraint, the discussion will focus on the effect of the gasification conditions on the amount of NH_3 in the gas phase based on the equilibrium reaction between NH_3 , N_2 and H_2 .

The experimental results are presented in the same way as the H_2S results. Each measurement is shown as (1) concentration of NH_3 in the fuel gas, (2) fraction of total fuel nitrogen released as NH_3 and (3) fraction of total fuel nitrogen released as NH_3 corrected for the carbon conversion. The results are grouped into three plots:

Figure 69 – Effect of gasification agent and temperature, Figure 70 – Effect of pressure and Figure 71 – Effect of different fuels.

8.4.2 Discussion

Effect of gasification agent and temperature:

Figure 69 shows two clear trends, firstly the increase of NH_3 concentration in the fuel gas with steam at temperature above 750°C and secondly a maximum of the NH_3 concentration at 850°C with maximum concentrations in the range of 1500 – 2500 vpm for the experiments with 100% CO_2 . These trends are also observed with data expressed as the total amount of nitrogen released as NH_3 . With steam at 850°C and 950°C between 30 and 40% of the nitrogen was released as NH_3 while at 750°C this value drops to 5 – 10%. The increase in NH_3 concentration with steam addition is well documented in the literature (2.4.7.2, page 59) and thought to be because of two reasons: (1) steam is hydrogenating the nitrogen in the coal and NH_3 is formed. (2) Steam addition increases the amount of H_2 in the fuel gas and can therefore move the gas phase equilibrium towards NH_3 . For the effect of gasification conditions four factors need to be considered: firstly, the difference in carbon conversion. Fuel nitrogen is mainly present as organic nitrogen and therefore combined within the carbon matrix and in the volatiles. Incomplete carbon conversion can therefore lead to nitrogen retention in the solid char and the resulting lower concentration of NH_3 in the fuel gas. This effect can be seen by comparing results of 750°C (low carbon conversion, 10% nitrogen released as NH_3) and of 850°C (high carbon conversion, 25% nitrogen released as NH_3). Adjusting these values for the differences in carbon conversion the amount released as NH_3 still increases with temperature, but the difference is much smaller (750°C : 25% and 850°C 30%). The second factor is the thermodynamic trend of NH_3 conversion into H_2 and N_2 , which increases with temperature. The third factor to consider is the increasing rate of reaction and therefore the measured concentration being closer to the thermodynamic equilibrium at higher temperatures. The fourth factor is the increased rate of reaction of NH_3 destruction via gas phase reaction. Therefore opposing trends with increasing temperature lead to a maximum of NH_3 release that 850°C as seen in the experimental data.

Effect of pressure: The results are presented in Figure 70. As discussed in chapter 6, page 149, the ratio between fuel and gasification agent for experiments carried out at 1 bar and at elevated pressure is different. Therefore, the trends in NH_3 concentration in the fuel gas on its own are misleading. However, analysing the total amount of nitrogen released as NH_3 , a clear trend with increasing pressure can be established: the amount of fuel nitrogen released as NH_3 increased with pressure. For example, at 1 bar in a steam/ CO_2 atmosphere 40% of fuel-

N is released as NH_3 , while at 15 bar 50% is released as NH_3 (values corrected for carbon conversion). As a result the concentration in the fuel gas increased from 1200 vpm to 1500 vpm. The increase with pressure can be related to the equilibrium between NH_3 , N_2 and H_2 , as increasing pressure moves the equilibrium towards more NH_3 . Overall, the trend with increasing temperature is comparable to the results found at atmospheric pressure, as with a temperature increase from 850°C to 950°C, the fuel nitrogen to NH_3 concentration decreases.

Effect of different fuels: The results are presented in Figure 71. For the two coals investigated, it can be seen that the concentration of NH_3 in the fuel gas is in a similar range (1000 - 2500 vpm) as well as the fraction of total nitrogen released as NH_3 (20 – 40%), if corrected for carbon conversion. This is despite the fact that DM contains twice the amount of nitrogen as GL (Table 17). However the form of fuel-nitrogen in DM and GL could be different and affecting the release. For the co-gasification of OB and GL, a fairly constant concentration of 2500 – 3000 vpm was measured in the fuel gas. However, calculating the fraction of fuel nitrogen released as NH_3 , it is found that, with increasing amount of OB, the conversion of fuel nitrogen to NH_3 is actually decreasing despite an overall increase in nitrogen content of the fuel. An explanation for this could be the preferential release of fuel-N as HCN. This could be a result of the difference in moisture content and therefore of the absence of hydrogen in the system. While GL contains 13.2% moisture, OB only contains 3.2% moisture. These experiments were carried out under CO_2 blown conditions and the only source of steam is the fuel moisture. As already discussed, steam is known to increase the fraction of NH_3 , as it can hydrogenate the fuel nitrogen.

Table 17: Nitrogen content of the fuels investigated in “as received basis”. Data taken from fuel analysis 3.3.3, page 89.

Sample	Daw Mill Coal	Coalite	Olive Bagasse	German Lignite	Polish Coal	
Nitrogen %	1.18	1.5	1.36	0.61	1.07	1.26

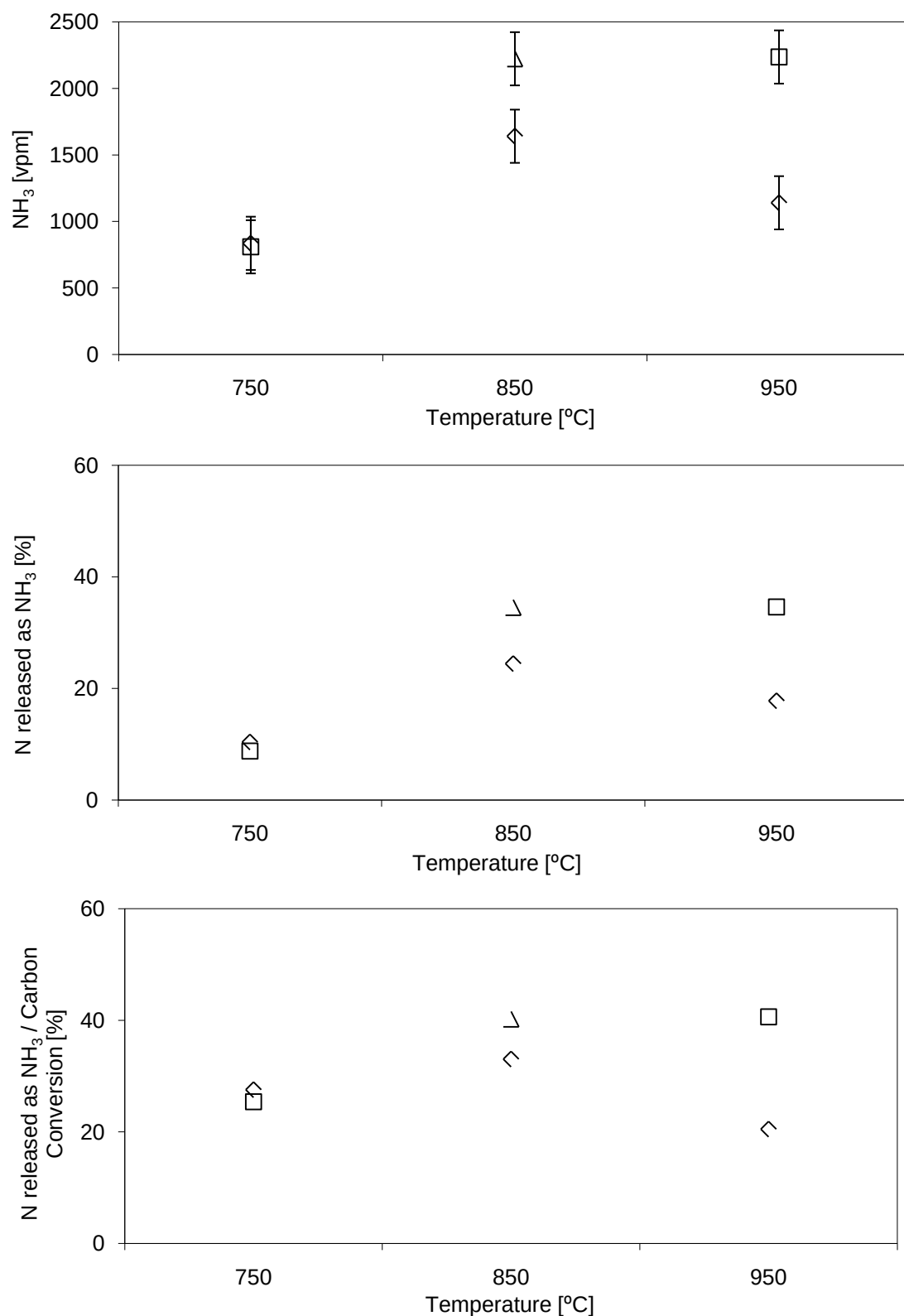


Figure 69: NH_3 in the fuel gas. Effect of gasification temperature and gasification agent. Top: concentration in the fuel gas, Middle: Percentage of sulphur releases as H_2S . Bottom Percentage of sulphur releases as H_2S corrected for carbon conversion. ($\diamond$ 100% CO_2 , $\square$ 25% Steam/ CO_2 , Δ 50% Steam/ CO_2)

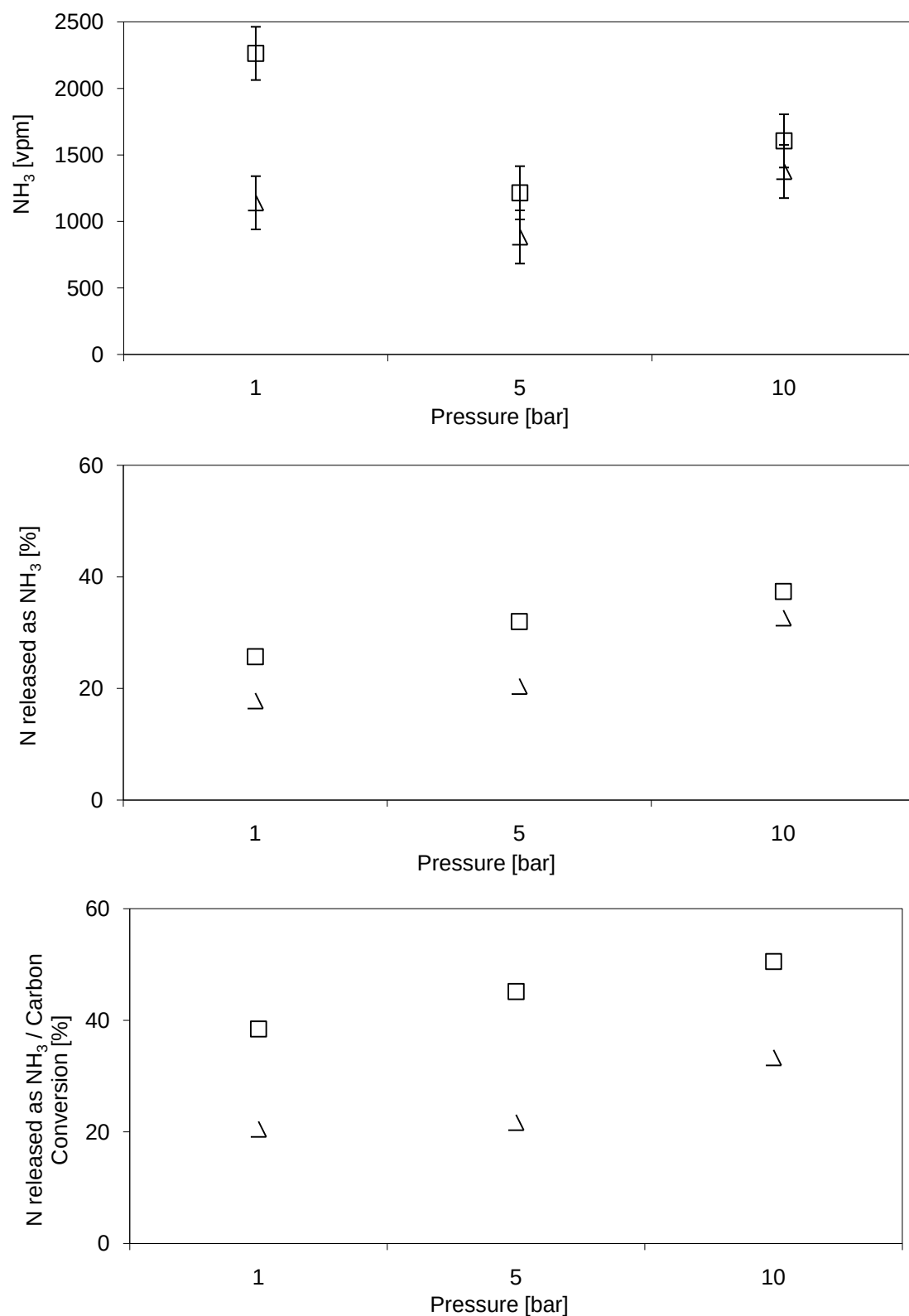


Figure 70: NH₃ in the fuel gas. Effect of Pressure. Top: concentration in the fuel gas, Middle: Percentage of sulphur releases as H₂S. Bottom Percentage of sulphur releases as H₂S corrected for carbon conversion. (□ O₂/CO₂ – 850°C, Δ O₂/CO₂ – 950°C)

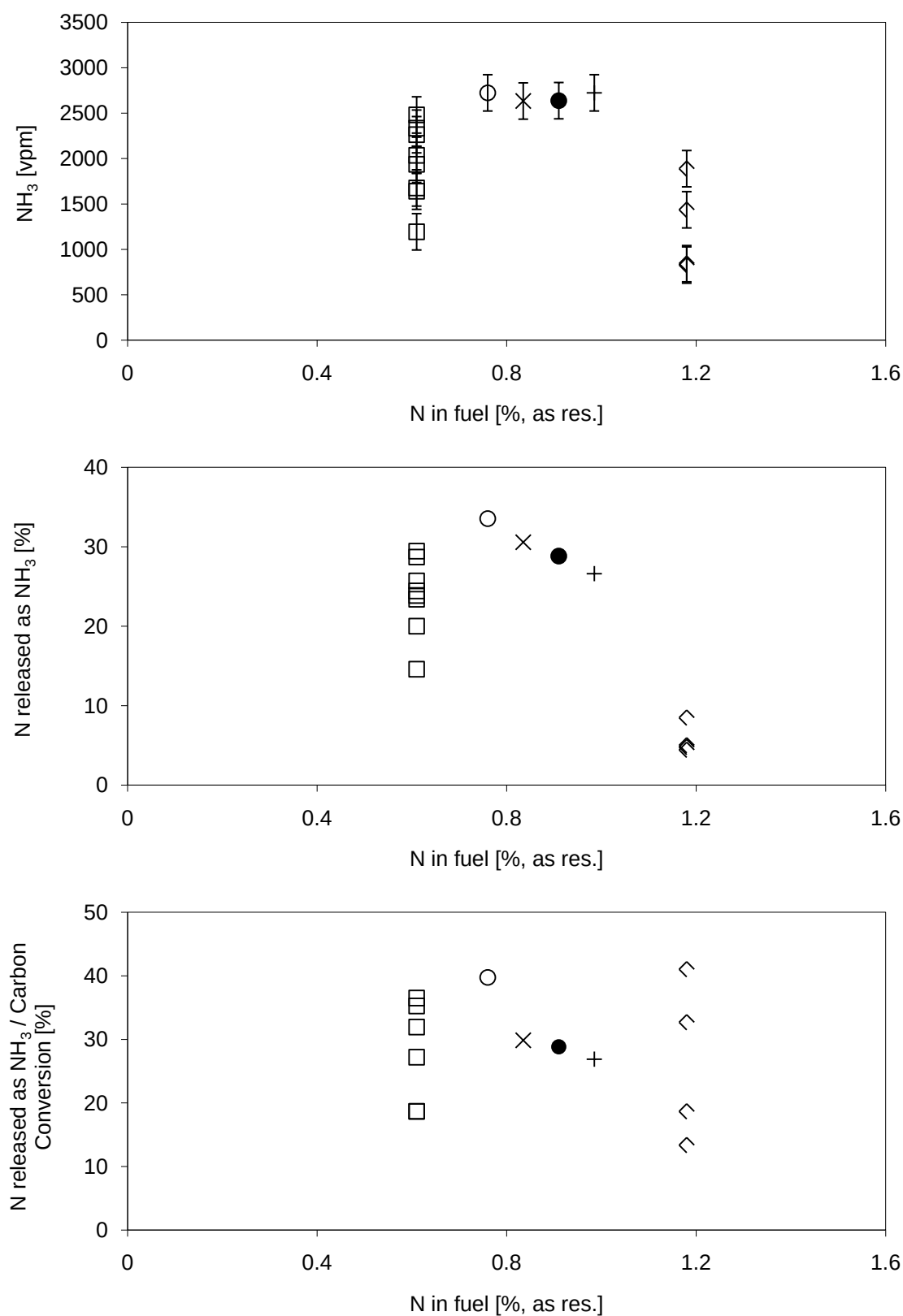


Figure 71: NH₃ in the fuel gas. Effect of Fuel. Top: concentration in the fuel gas, Middle: Percentage of sulphur released as H₂S. Bottom Percentage of sulphur releases as H₂S corrected for carbon conversion. (all experiments at atmospheric pressure - ◇ Daw Mill Coal (10% O₂/CO₂, 850°C, different fuel feeding rate), □ German Lignite (O₂/CO₂, 850°C, different O/C ratio), OB/GL Mixture (○ 20% OB, x 30% OB, • 40% OB, + 50% OB - 100% CO₂, 850°C))

8.4.3 Conclusions

The findings about the NH_3 release can be summarised in three main points: (1) Steam was confirmed to increase the amount of fuel nitrogen converted to NH_3 . Furthermore differences in moisture content of the fuel during co-gasification were identified as the most likely reason for the differences in fuel nitrogen to NH_3 conversion. (2) With increasing temperature the NH_3 concentration is mainly affected by two factors (if the results are corrected for conversion): firstly the exothermic gas phase conversion of NH_3 and secondly the faster rate of its formation. In this set of experiments that leads to a maximum in the amount of NH_3 released at 850°C . (3) The NH_3 release increases with pressure. The reason is thought to be the shift in the NH_3 , N_2 and H_2 equilibrium. The decrease in NH_3 release in the temperature range from 850°C to 950°C could be confirmed at elevated pressure.

8.5 Summary

In this chapter three minor fuel gas constituents of the gasification process and the effect of operation conditions on their release have been discussed. The aim of the investigation was to increase the understanding of the processes involved and estimate the potential emission from an oxy-fuel fluidised bed gasification process.

Tar Release: The results have shown the advantages of a bottom fed spouted bed design in terms of tar cracking. It has been shown that all the tar released from the fuel was destroyed while passing through the carbon containing bed. Furthermore the increased extent of tar cracking, with increasing pyrolysis temperature, as well as the extent of volatile combustion by O_2 could be shown. Additional analysis of the tar provided information about the difference in molecular size distribution and aromatic chromophores.

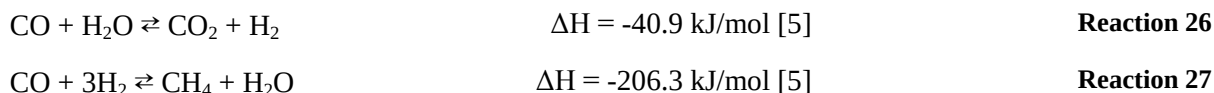
H_2S and NH_3 release: The analysis of the NH_3 and H_2S release have two main implications for a large scale oxy-fuel fluidised bed process: (1) steam addition increases the concentration of H_2S and NH_3 in the fuel gas. In comparison to an air blown or oxygen/steam blown process, the proposed oxy-fuel process would be operated without the use of steam. Based on these results, this would reduce emission of sulphur and potentially nitrogen compounds; (2) the high partial pressure of CO_2 in an oxy-fuel process requires an increased bed temperature for efficient in-bed sulphur retention by $CaCO_3$. Results have shown the effect of sulphur retention by the fuel ash, as well as for the sulphur retention by added dolomite.

9 Thermodynamics

9.1 Introduction

The general thermodynamic trends for the gasification process have already been discussed briefly in 2.4.3, page 46. In this chapter these trends are analysed in more detail by calculating the thermodynamic equilibrium composition of the fuel gas at the conditions prevailing in the laboratory scale reactor. The chapter is divided into two sections. Section 1 discusses the general trends for the equilibrium of a C-H-O system and the ranges in which the gasification process operates (steam and CO₂ gasification). In section 2, the measured fuel gas compositions are compared with calculated equilibrium values and the results are used to discuss if and how the data can be used to predict the performance of a gasifier.

Equilibrium calculations for the C-H-O gas phase system have been carried out using the method described in Appendix D.1, considering only the major fuel gas constituents (CO, CO₂, H₂O, H₂ and CH₄) and the two major gas phase reactions, water-gas shift (Reaction 26) and steam reforming (Reaction 27).



It has to be noted that the discussion in this chapter is based on thermodynamic equilibrium only. No considerations of the kinetics of the reactions are made. It is therefore a theoretical assessment and is based on the assumption of a C-H-O system with a sufficient residence time to reach equilibrium.

9.2 Thermodynamics of Gasification

The thermodynamic situation in a C-H-O gas phase system depends on the conditions (pressure and temperature) and the concentrations of C, H and O in the system. Four different regions can be distinguished in a three component diagram (Figure 72). In region I, an excess of C is available. The amount of H and O is less than what would be required for all C to be in the form of CO, CO₂ or CH₄. To the left of the heterogeneous equilibrium line, CO/CO₂ and H₂/H₂O co-existed in the gas phase, in region II, enough O and H is theoretically available to convert all C to CO/CO₂/CH₄. The soot boundary separates region II from region III where all C is in the gas phase. The position of the soot boundary is a function of pressure and temperature. To the left of the homogeneous equilibrium line, O is in excess and only H₂O, CO₂ and O₂ can be present. The region of a gasification process is between the heterogeneous and the homogenous equilibrium, whereby it is desirable to have as little CO₂ and H₂O present as possible (in the diagram towards C) while on the other hand ensuring that all available C is in the gas phase (complete carbon conversion, in the diagram towards O and H).

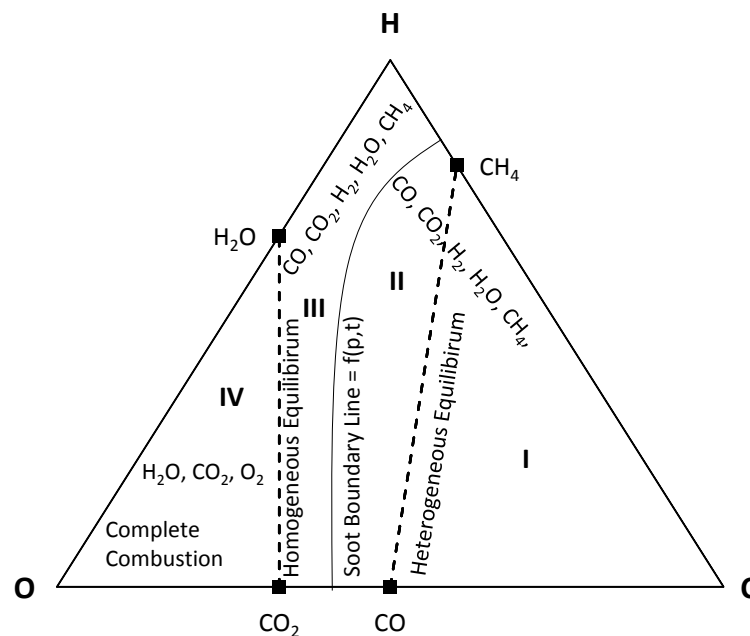


Figure 72: Thermodynamic of Gasification: C/H/O System – Different Ranges: (I) C – Excess, (II) Soot – Range, (III) Soot – Free Range, (IV) O₂ – Excess. [6]

The situation in the laboratory scale reactor in the form of a C-H-O system in a three component diagram is shown in Figure 73. In the right corner, the range of hydrocarbon fuels and the position of the fuels used in this project are shown. In the bottom right corner would be graphite followed by anthracite, bituminous and sub-bituminous coal, as the content of first hydrogen and then oxygen increases and the coal rank decreases. From the graph it can be seen that DM and PC are quite similar in terms of their C-H-O contents, while OB and GL have the same hydrogen content and OB has the highest O content, as is typical for biomass. The C-H-O content of the fuels was calculated using the data from the ultimate analysis (3.3.3, page 89). The hydrogen and oxygen from the moisture was included, as it will be released into the gas phase in the gasifier and affect the position of the thermodynamic equilibrium. In Figure 73 the areas for steam and CO₂ gasification are marked assuming a steam/C and CO₂/C ratio of 1/1 without oxygen added to the system. It can be seen that depending on the type of gasification agent the position of the C-H-O system in the three component diagram is different. Both areas have the same C/O ratio, but in steam gasification the H/O and H/C ratios are much higher. The effects these differences have on the position of the thermodynamic equilibrium are presented in the next section.

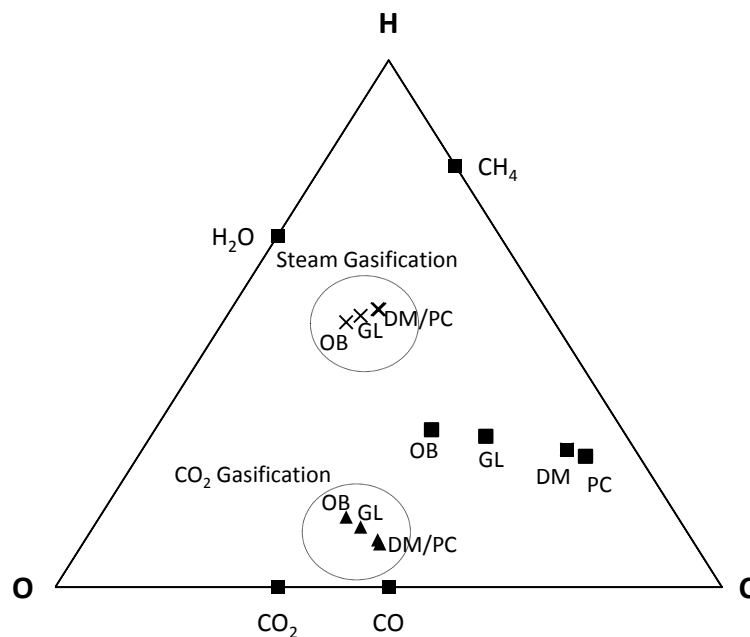


Figure 73: Thermodynamics of Gasification: C/H/O System – Range of fuels and range of CO₂ and steam gasification

To calculate the thermodynamic trends, with changing temperature and pressure, for steam and CO₂ gasification, the average ratio of C:H:O for all four fuels is taken. The values used for the calculation are shown in Table 18.

Table 18: C:H:O ratio for different fuels and steam/CO₂ gasification (Values for steam and CO₂ gasification calculated with a steam/C and a CO₂/C ratio of 1 and no added oxygen).

	OB	GL	PC	DM	Average	Steam gasification	CO ₂ Gasification
C	1	1	1	1	1.0	1.0	2.0
H	0.72	0.57	0.37	0.41	0.5	2.5	0.5
O	0.69	0.42	0.13	0.16	0.3	1.3	2.3

The results of the equilibrium calculation in the temperature range from 650°C to 1000°C and for 1 and 20 bar are shown in Figure 74. The top row shows the steam gasification and the bottom row the CO₂ gasification. Two observations can be made straightaway: (1) The position of the equilibrium in steam gasification is more dependent on temperature than in the case of CO₂ gasification. (2) In both cases the position of the equilibrium is more dependent on temperature at 20 bar than at 1 bar. These effects can be explained by the characteristics of the gas phase reactions: The water-gas shift reaction is only slightly exothermic, while the formation of CH₄ is strongly exothermic. The steam reforming reaction however is only important in the steam gasification as, compared to CO₂ gasification, the amount of hydrogen in the system is much higher - therefore the position of the equilibrium in the steam gasification case is more temperature dependent. Similar for the case of increasing pressure: only the equilibrium of the steam reforming reaction is dependent on pressure and therefore the temperature dependency increases with increasing pressure.

For the temperature range considered in the experimental work for this project (750°C – 950°C), the position of the equilibrium in the case of steam gasification shifts slightly toward CO and H₂O with increasing temperature due to the exothermic WGS reactions. For CO₂ gasification the gas phase composition is virtually invariant in this temperature range for atmospheric pressure. In this case the low amount of input hydrogen dominates the position of the equilibrium. Only for steam gasification at 20 bar is a significant amount of CH₄ predicted. For all other cases, the concentration of CH₄ above 750°C is very low.

At 1000°C approximately 80% of the gas phase consists of H_2 and CO , whereby the H_2/CO ratio for steam gasification is about 1:1 while for CO_2 gasification, CO is the dominating species.

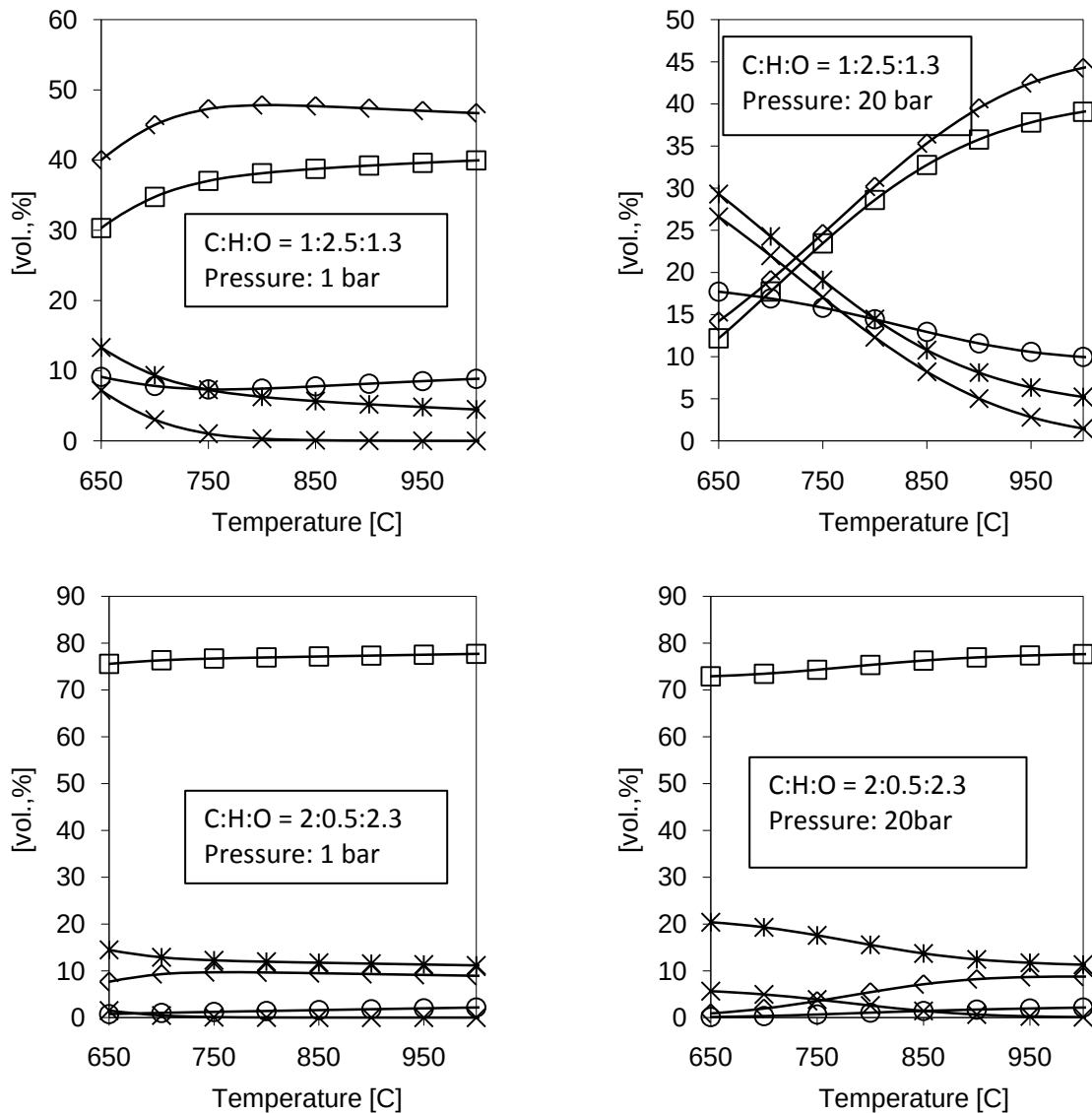


Figure 74: Thermodynamic trends for steam gasification (top left 1 bar, top right 20 bar) and CO_2 gasification (bottom left 1bar, bottom right 20 bar). □ CO, * CO_2 , ◇ H_2 , ○ H_2O , × CH_4

9.3 Comparing the Results of the Laboratory Scale Reactor with Thermodynamic Calculations

In the previous section the position of the equilibrium at different temperatures and pressures for steam and CO_2 gasification were calculated. In this section, the measured fuel gas

compositions are compared with results of equilibrium calculations. The equilibrium is calculated using the method described in Appendix D.1. For the calculation it is assumed that all H and O from the fuel and the gasification agent goes to the gas phase. The amount of C in the gas phase is calculated by assuming all carbon injected as CO_2 is in the gas phase plus the carbon of the fuel, corrected for the experimental carbon conversion. The calculated data are converted to a 'dry basis' to enable them to be compared directly with the measured data. Two different sets of experiments have been compared: (1) different temperatures and steam/ CO_2 ratios shown in Figure 75 and (2) different pressures shown in Figure 76. The following observations can be made.

Concentration of CH_4 in the fuel gas: As discussed before, the concentration of CH_4 predicted by the equilibrium calculations is very low, while the experimental values are in the range of 1 – 3 %. This confirms the assumption that CH_4 is solely a product of pyrolysis under these conditions and not formed or destroyed in the gas phase.

Temperature: From Figure 75, it seems that at 950°C the gas phase is in thermodynamic equilibrium (indicated by the coincidence of the calculated and experimental points). With decreasing gasification temperature the measured gas phase composition deviates from the calculated equilibrium values. At higher temperatures, the gas phase reactions are fast enough to reach equilibrium, before the gas leaves the reactor and the composition is 'frozen' in the cooled tar trap. At 850°C, the calculated data still predicts the trends very well; however the equilibrium values are up to 5% (abs.) different from the measured data. In general the concentration of CO is over predicted, while CO_2 is under predicted.

Steam/ CO_2 ratio: It can be seen that with changing steam/ CO_2 ratio, the difference between calculated equilibrium and measured fuel gas compositions does not change.

Pressure: The calculated data follow the same trend as the measured data with increasing pressure. However it seems that at higher pressure, the gas phase in the reactor does not reach equilibrium anymore. One possibility could be that the gas phase concentration is not immediately 'frozen' after leaving the reactor. The very high flow rates of the fuel gas make it more difficult to quench the reactions. Therefore the gas phase is at a lower equilibrium temperature than the reactor temperature.

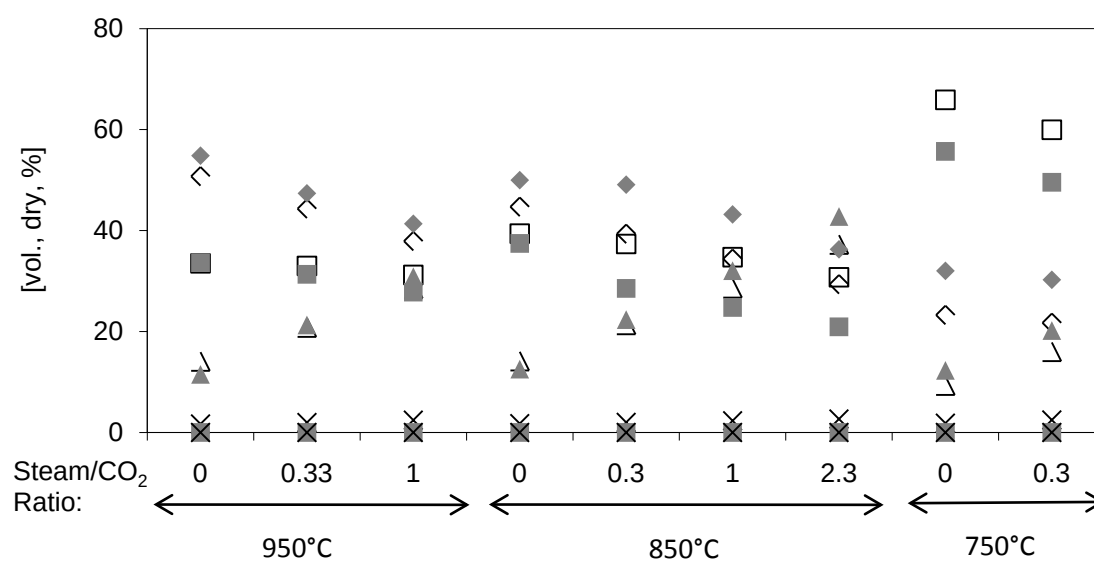


Figure 75: Comparing experimental data with thermodynamic equilibrium: GL, different steam/CO₂ ratios (□ CO₂, ◇ CO, Δ H₂, × CH₄ - ■ calculated □ measured).

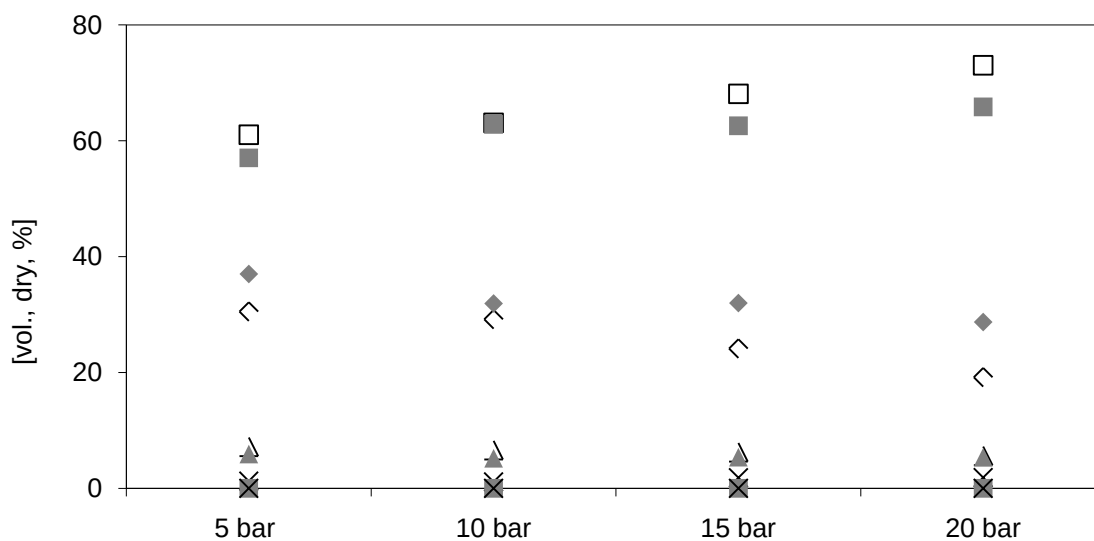


Figure 76: Comparing experimental data with thermodynamic equilibrium: 850°C, GL, 5 – 20 bar pressure, 3.7% O₂/CO₂ (□ CO₂, ◇ CO, Δ H₂, × CH₄ - ■ calculated □ measured).

9.4 Summary

In this chapter the thermodynamic equilibrium trends for the major fuel gas components have been investigated. From the analysis it is clear that the equilibrium trends for the fuel gas composition can be very different depending on the C:H:O ratios. The following conclusions can be made:

- (1) It was shown that general assumptions about the equilibrium trends in gasification processes as presented in 2.4.3, page 46, can be misleading if the basis of the calculation, the C:H:O ratio of the system, is not clearly stated. For example the assumption that with increasing temperature the H_2 content of the fuel gas increases was found to be true only for selected cases. For example in the case of steam gasification at atmospheric pressure shown in Figure 74, the concentration of H_2 in the fuel gas actually decreases with increasing temperature above 750°C .
- (2) The equilibrium trends of steam gasification and CO_2 gasification were found to be different. It seems that only at elevated pressure the equilibrium fuel gas composition of a CO_2 gasification process changes significantly with temperature. At atmospheric pressure, it was almost invariant. In comparison, the equilibrium fuel gas composition from a steam gasification process was found to change with temperature at both, atmospheric and elevated pressure.
- (3) Comparing the measured fuel gas composition with the calculated equilibrium composition, it was found that at 950°C the gas leaving the laboratory scale gasifier is in thermodynamic equilibrium. At lower gasification temperatures, equilibrium fuel gas composition is not reached under the conditions investigated.
- (4) From these findings it can be concluded that equilibrium calculations can be used to predict the performance of spouted bed gasifier under oxy-fuel conditions if the gasification temperature is high and the carbon conversion is either known or can be assumed to be complete.

10 Design Implications of the Results

10.1 Introduction

The project has shown that the oxy-fuel spouted bed process is, in principle, a feasible process option, but further development/testing is needed prior to committing to commercial scale application. In a next step, testing at pilot scale will be necessary to establish if the good performance of the laboratory scale process can be obtained on a larger scale. To assist further development, the data about gasification performance and operability of an oxy-fuel spouted bed gasifier gained using the laboratory scale reactor are used to provide recommendations on reactor design and conditions to be used for larger scale oxy-fuel gasification developments. First, the limitations of the laboratory scale reactor are discussed and used to derive the key requirements for the pilot scale before design recommendations are given.

10.2 Limitations of the Laboratory Scale Reactor and Resulting Key Requirements of the Pilot Plant

10.2.1 Bed height control

The main disadvantage of the small scale reactor is the absence of a means to remove solids from the bed during gasification. Despite this, a steady state fuel gas composition was reached, with the bed composition and the bed height changing over the duration of each experiment. Both parameters could influence the gasification performance, as the inorganic and potential catalytic content of the bed changed as well as the gas residence time. A larger scale reactor should include a system to remove solids from the bed. This would make it possible to analyse the amount of unconverted carbon in the ash and to keep the bed composition and height constant.

10.2.2 Solid Back Mixing and Gas Solid Contact

Due to the small diameter of the reactor (28 mm), it is possible to test the gasification performance over a very large range of conditions in a well defined environment. However, the small diameter negatively influences the solid mixing and gas solid contact in the bed. The conical section of the reactor designed to encourage solid back mixing was found to have a dead zone near the spout which encouraged build up of agglomerated material. The bed

area above the submerged spout behaves as a bubbling fluidised bed. The small diameter increases the tendency for slugging and therefore reduces gas solid contact. This could be a reason for the finding in 5.2.3, page 139, where no effect of gas residence time on the carbon conversion was found. In a pilot scale reactor with a typical diameter of 0.3m the hydrodynamical conditions can be better defined and controlled resulting in a better gas solid contact regime and elimination of dead zones.

10.2.3 Heating

The laboratory scale reactor is heated externally by resistance heating of the reactor shell. This on the one hand makes it possible to investigate the gasification reactions at different temperatures independently of the oxygen fuel ratio (O/C ratio in this project), but on the other hand makes it very difficult to judge the oxygen demand of a oxy-fuel process. For a pilot scale reactor, the heat loss through the reactor wall is still larger than for a full scale reactor, but it is easier to quantify the effect and electrical heating can be used to compensate more accurately for the lost energy. As a result, a pilot plant would be effectively heated auto thermally by combustion of fuel. This would reduce the range of possible conditions but enable precise measurement of oxygen demand and therefore give more a realistic picture of the energy conversion.

10.3 Reactor Design

Base design: The reactor configuration used in this project was a spouted bed reactor with a submerged spout in the bottom part and a bubbling fluidised bed in the top part of the reactor. A single spout jet, sited at the apex of an inverted cone shaped base has been shown to be effective in air/steam and oxygen/steam blown gasifiers [131, 133]. The included angle of the cone should be between approx 30 and 60 degrees and there should be small jets in the surface of the cone. The cone jets encourage slippage down the cone surface and ensure effective recirculation of the bed material down the cone and into the spout. The actual detail of the base, optimum included angle and configuration of the cone jets should be developed by cold model studies. It is also possible that multi spouts may be needed for large diameter reactors.

Feed position: In this study fuel was fed through a spout jet. This configuration ensured rapid particle heating and conversion. In addition the tar particles are more likely to be destroyed in

the bed as they are created at the bottom and pass through the whole length of the bed which will maximise the extent of cracking. This was demonstrated in the project (8.2, page 176). Feeding fuel through the spout has also several other advantages including:

- (1) Possible sticky fuel particles will be rapidly mixed with non sticky bed particles.
- (2) N released as NH_3 , can equilibrate to N_2 and H_2 via a gas phase reaction as the residence time is maximised by the base feeding.

If co firing coal with biomass is required, then the feeds can be premixed, or more conveniently, metered separately into the spout.

Control of bed height: The spouted bed configuration offers a very attractive method of removing unreactive and unreacted material from the bed. An annular pipe is built around the spout in a way that de-fluidised/agglomerated/sintered material is removed at the lowest point of the bed by gravity. The rate of bed material discharge can be controlled by a rotary valve.

Reactor diameter: In general the diameter defines the energy output of the gasifier. For a pilot scale installation it is a compromise between capital costs and the desire to simulate the conditions of a full scale reactor as close as possible. A typical diameter of pressurised pilot plant is 0.3 m. For a commercial application of the oxy-fuel process, only a large scale gasifier will be attractive because of the capital and operational cost of the air separation unit.

Bed material: Reactive fuels, like lignite or biomass with low ash content, will require an additional bed material, while lower reactivity materials, such as bituminous coals or fuels with very high ash content will, probably produce enough unreacted char/inorganic material to form a viable bed. Depending on the fuel and on the requirement for sulphur retention a number of different materials are possible, including silica sand, Al_2O_3 , dolomite and limestone. In this project, it was shown that silica sand can react with the inorganic material of some fuels (4.3.3.3, page 118) and this can cause operational problems. In addition, it was shown that dolomite can be used to retain sulphur and has a catalytic effect on the gasification reactions. Based on this study, dolomite would be recommended for the processing of German lignite. Laboratory scale reactors can be used to test further fuel/bed material combinations similar to the work done here.

10.4 Fuel

German Lignite has been found to be a reactive fuel under oxy-fuel gasification conditions and there is potential to achieve high fuel and energy conversions at the large scale, using relative moderate, realistic temperatures for a fluidised bed gasifier. Therefore, reactive lignite is the recommended fossil fuel. Bituminous coals are less reactive and this limits the fuel conversion and introduces the problem of what to do with unconverted C, without emitting CO₂ to the environment. The fuel conversion of the two bituminous coals tested, Polish and Daw Mill coal was only ¼ of the conversion achieved with the lignite. The successful processing of bituminous coal would require a higher temperature, possibly in the ash agglomeration regime, the partial replacement of CO₂ with the more reactive steam and use of catalytic bed material.

The impact of biomass co-firing depends on the nature of the biomass and its proportion in the fuel mix. The co-gasification of German Lignite and Olive Bagasse was tested in this project and found to be a viable option. It was possible to keep the gasification performance constant, while coal was replaced with biomass. In addition it could be shown that the inorganic material in the biomass reduced the emission of H₂S. Overall biomass co-processing reduced the fossil CO₂ emission per unit energy output and utilised a waste product. However, due to the low energy density of biomass the use as fuel for centralised large scale plants is limited.

10.5 Gasifier Operating Conditions

Temperature: For coal gasification in a fluidised bed, normally the temperature is chosen as high as possible, within the limit set by the ash melting/softening properties to avoid agglomeration and de-fluidisation. In this project German lignite was successfully gasified in the range of 850 – 950°C. At the lower end of the temperature range, either part of the CO₂ had to be replaced with steam or the CO₂/C ratio had to be increased to achieve gasification performance comparable to 950°C. High temperature is normally required to ensure maximum carbon conversion, however higher temperatures also require more oxygen and lower the energy conversion as more carbon is converted into CO₂. Therefore, lowering the temperature, while keeping the performance constant can help to optimise the overall plant performance. An additional factor to consider is sulphur retention: Oxy-fuel conditions were

found to increase the temperature at which sulphur can effectively be retained by limestone/dolomite because of the high partial pressure of CO_2 (8.3.5, page 192).

Gasification Agent: The gasification agent in an oxy-fuel process consists of O_2 , CO_2 and if necessary steam. The study carried out (4, page 108) on the effect of CO_2/C ratio and steam/ CO_2 ratio on the carbon and energy conversion provides a good starting point to select the ratio of gasification agent to fuel and to see whether steam can be used to optimise the process. In the previous chapter (9, page 203), it was shown that at high temperature the experimental fuel gas composition corresponded to the calculated thermodynamic gas phase equilibrium composition. Therefore, the required amount of O_2 for a pilot scale plant could be easily estimated by making a heat balance between the heat and energy content of the fuel gas, the heat loss through the reactor wall and the heat value of the fuel gas.

Pressure: The application of oxy-fuel gasification would be mainly for power generation via an IGCC and to a smaller extent chemical synthesis (low H_2 content of the fuel gas might be problem). The required air separation unit would allow efficient operation only on a very large scale and high throughput. Together with the efficiency improvement by using high pressure fuel gas for the gas turbine and for the CCS process, operation pressure would be in the range of 2-4 MPa. The pressure of a potential pilot plant would be as close as possible to this range, but limited by the capital costs. This study showed that increasing pressure and at the same time increasing the fuel throughput can lead to particle-particle interaction negatively affecting fuel conversion. This clearly indicates that the pilot plant should operate at a similar pressure and throughput/diameter ratio as the full scale plant to produce viable design data. High pressure might require a higher reactive gasification agent or higher temperature to achieve comparable gasification performance compared to atmospheric pressure.

11 Conclusions and Recommendations for Future Work

11.1 Conclusions

Three main objectives were defined at the beginning of this project: (1) to modify an existing spouted bed reactor to work under oxy-fuel conditions and with continuous fuel feeding. (2) to carry out an experimental study to establish the gasification performance and operability of different fuels under oxy-fuel conditions and to judge the feasibility of the oxy-fuel process configuration and (3) to use the information to derive design recommendations for a larger scale testing facility. The main conclusions of the project are summarized as follows:

- (1) **Reactor construction, modification and commissioning:** An existing bench scale, spouted bed reactor has been successfully modified to gasify a range of fuels under oxy-fuel conditions. The modification and improvements included:
 - Modifications to the resistance heater: (1) Integration of a variable transformer to enable different electrode positions and extend the range of possible fuels. (2) Redesign of the floating bottom electrode and (3) adding cooling for the bottom electrode to prevent the cables from over heating due to the increased power demand under oxy-fuel conditions.
 - Installing mass flow controllers to accurately adjust the fluidising gas composition and flow rate.
 - Design of a steam generator and steam injector to enable continuous operation with steam as gasification agent.
 - Redesign of the continuous fuel feeder to improve feeding and prevent blockage which comprised: (1) direct connection of the main feed hopper to the rotary valve and (2) newly design rotary valve to enable feed rates up to 6 g/min.
 - Design of a new tar trap to cool the fuel gas stream with ice/water mixtures instead of liquid nitrogen to prevent condensation of CO₂.
 - Installing a dry gas meter to measure the volumetric fuel gas flow rate.
 - Design and development of a computer based temperature controller.
 - Integration of temperature control, online gas analysis and data acquisition in a newly developed Labview-based software.

- (2) **Operability:** In this project two major problems with the operability in the oxy-fuel gasifier were identified: (1) Sand-ash agglomeration at high gasification temperatures, with German lignite and subsequent loss of fluidisation. (2) Fuel agglomeration with Daw Mill coal, Polish coal and Olive Bagasse at the top of the spout line. Both effects were not strictly related to the high partial pressure of CO_2 under oxy-fuel conditions. The agglomeration of ash and sand is a result of the formation of low melting silicates of Na and K and is a well known phenomenon in fluidised bed operation. No agglomeration was observed with fuels with low Na and K content (e.g. Daw Mill coal) or with dolomite as bed material. From the experiments carried out here, it is not possible to judge if the effect is enhanced by high partial pressure of CO_2 . The agglomeration of fuels in the spout line on the other hand, was observed under nitrogen atmosphere and CO_2 atmosphere. This rules out high partial pressure of CO_2 as the cause. Most likely it is caused by changes of the inorganic material during heat up.
- (3) **Pyrolysis and Partial Oxidation:** Experiments were carried out in the temperature range from 750 – 950°C under atmospheric pressure either with N_2 or with 10% O_2/N_2 . It was found that with German lignite, the carbon conversion under pyrolysis conditions increased almost linearly from 25 – 40% with temperature. The majority of the carbon was released as CO and at 950°C the CO/ CO_2 ratio of the fuel gas corresponded to the Boudouard equilibrium. Using 10% O_2/N_2 a 10% increase in carbon conversion was noted together with a decrease in CO/ CO_2 ratio due to the combustion reaction. The amount of hydrogen increased with temperature, while the amount of CH_4 in the fuel gas was fairly constant.
- (4) **Temperature:** The effect of temperature on the gasification performance was investigated in the range from 750 – 950°C. Increasing temperature increased carbon and energy conversion. Complete carbon conversion was achieved at 950°C, atmospheric pressure and German lignite, under all conditions investigated except with high levels of oxygen as this caused agglomeration of bed material (see above). It was found that the same gasification performance (carbon and energy conversion) could be achieved at 850°C if: (1) a higher CO_2/C ratio was used ($\text{CO}_2/\text{C} = 1.8$ as

opposed to 1.0), (2) 25% of the CO₂ were replaced with steam, and (3) dolomite as catalytic bed material was used. At 750°C almost no char-CO₂ gasification took place. These findings showed on the one hand that with lignite as fuel, the gasification performance at 850 – 950°C under oxy-fuel conditions was promising and on the other hand how plant efficiency could be increased by decreasing the operating temperature and therefore reducing the oxygen demand and increasing the energy conversion.

(5) **Gasification Agent:**

Oxygen – O₂ was mixed with N₂ or CO₂ at a concentration of up to 10% (O/C ratio = 0.2). Adding oxygen increased the carbon conversion as the char-O₂ reaction under these conditions is very fast and always complete. For O₂/N₂ mixture, it was found that the CO/CO₂ ratio of the char combustion increased with temperature while for O₂/CO₂ mixtures it decreased. For oxy-fuel gasification at 750°C increasing the amount of O₂ increased the energy conversion as part of the O₂ reacts with carbon to form CO, while at 850°C almost all O₂ was found to form CO₂ and no increase in energy conversion was noted, despite an increase in carbon conversion. At 950°C, high levels of O₂ were found to cause agglomeration of bed material (see above). This reduced the mixing of the bed material and carbon conversion actually decreased with increasing amounts of O₂ in the fluidising gas.

Carbon Dioxide - CO₂ was used as the main gasification agent. In the beginning of the project the power of the resistance heater had to be increased to enable gasification under high partial pressure of CO₂ due to its high heat capacity. The second main modification necessary was the re-design of the tar trap to use ice instead of liquid N₂ as cooling agent to prevent the condensation of CO₂. Despite the relatively slow CO₂-char reaction, good gasification performance could be achieved with German lignite: complete carbon conversion, high energy conversion and a medium heating value fuel gas (8 – 10 MJ/m³). The CO₂/C ratio was found to have a large effect on the gasification performance. Increasing the ratio increased the carbon conversion, but the CO₂ conversion decreased. A Langmuir Hinshelwood type

of rate equation was qualitatively confirmed for the char-CO₂ reaction including the inhibiting effect of high CO concentrations.

Steam – H₂O was used to replace up to 70% of the CO₂ as gasification agent. At 950°C, maximum carbon conversion was already achieved with pure CO₂ and using steam was found only to increase the H₂/CO ratio of the fuel gas. At 850°C, replacing 25% of CO₂ with steam increased the carbon conversion to the level achieved at 950°C. Replacing more than 25% of CO₂ with steam increased the H₂/CO ratio further. A Langmuir Hinshelwood type of rate equation was qualitatively confirmed for the char-steam reaction. However in the range investigated, no inhibiting effect of H₂ was detected and the steam conversion was constant at 40%.

- (6) **Gasification pressure:** It was found that increasing the pressure from 5 to 20 bar decreased the carbon conversion from 73% to 54%, while energy conversion and fuel gas heating value followed a similar trend. The results of high pressure pyrolysis and gasification in the fluidised bed reactor were compared to wire mesh reactor data. It was found that for pyrolysis, the total volatile yield of the wire mesh reactor was comparable with the steady state gas yield of the fluidised bed reactor. This indicated that even under pyrolysis conditions the majority of the tar was destroyed in the bed. For gasification, it was found that carbon conversion in the wire mesh reactor was 10% higher between 5 and 10 bar and increased with pressure. For the fluidised bed reactor, carbon conversion decreased with pressure, while the values at 5 and 10 bar were comparable with wire mesh data for 10 s holding time. It is proposed that due to the higher fuel/char particle density in the fluidised bed at high pressure (fuel feeding rate was increased with increasing pressure to keep the ratio between fuel and gasification agent constant and to simulate the increase throughput with high pressure), tar from fuel particles undergoes secondary reactions with other fuel particles. This results in the deposition of unreactive secondary char on the primary char surfaces and reduces the overall reactivity as the pressure is increased. Strategies developed under atmospheric pressure operation were used to increase the gasification performance at elevated pressure. Increasing the gasification temperature to 950°C, increasing the CO₂/C ratio and replacing part of CO₂ with steam were identified as possible ways of increasing the performance. The results show that with a

combination of these strategies, good gasification performance could be achieved under elevated pressure.

- (7) **Bed Material and Bed Size:** In the majority of the experiments 60 g of silica sand was used as initial bed material. A number of experiments were carried out with a smaller initial bed and it was found that the carbon conversion increased with decreased bed weight. This was despite the fact that in initial cold tests the best solid back mixing was observed with 60 g of initial bed material. It was concluded that the high char/sand ratio in experiments with less than 60 g sand was the main reason for the improved gasification performance. To confirm this, a set of experiments was carried out in which char was added to the initial bed. It was found that adding char to the bed (up to 2.5 g) increased the carbon conversion. This confirmed the previous assumption that the char/sand ratio in the bed was the main factor. A number of possible reasons for this were identified: Improved solid mixing in the char bed, enhanced volatile destruction in the char bed and potential catalytic activity of the inorganic material, as high char/sand ratio also meant more inorganic fuel material. Dolomite in the initial bed was found to increase gasification performance. At 850°C with 60% dolomite in the bed complete carbon conversion was achieved and the gasification performance was comparable to the results at 950°C. This was an effect of the catalytic activity of CaO towards the gasification reactions.
- (8) **Fuels:** The majority of the experiments were carried out with German lignite as fuel. To test the gasification performance of an oxy-fuel fluidised bed with higher rank fuels, two bituminous coals, Daw Mill and Polish coal, were tested. Besides the operational problems with the bituminous coal described above, the carbon conversion was approximately 50% lower. It was concluded that before higher rank coals can be considered for fluidised bed oxy-fuel processing, the carbon conversion needed to be optimised. This study identified a number of possible ways which could be used to successfully process bituminous coal: increasing the gasification temperature, increasing the CO₂/C ratio, replacing part of the CO₂ with steam and using catalytic bed material. Up to 50% (by weight) of biomass (olive bagasse) was co-processed with German lignite. It was found that at 30% OB/GL carbon conversion reached 100% due to the high char reactivity and the lower carbon content

of the biomass. The H_2 concentrations in the fuel gas decreased slightly with biomass co-feeding, mainly because of the lower moisture content of OB (3% compared to 13% in GL). At the same time the CH_4 content increased. It was concluded that co-feeding of biomass is a viable option to use waste for power generation and further reduce the carbon footprint of an oxy-fuel process.

(9) **Emissions:**

Tar – In this project, tar was collected by cooling the fuel gas stream, directly after the reactor, to room temperature and collect the condensed hydrocarbons by washing the tar trap with solvents. The key finding of the tar measurements was that tar was effectively destroyed in a bed containing at least 2 – 5 g of carbon. This was shown by two different approaches: (1) The same amount of tar was collected from experiments with different durations. It was concluded that tar only is released from the fuel particles into the fuel gas stream during start up when the bed did not contain any carbon. (2) The gas yield from the fluidised bed reactor was comparable to the total volatile yield measured with the wire mesh reactor under elevated pressure. For co-processing with biomass it was found, that the tar released during start up increased with increasing amount of biomass in the feed. Two reasons were identified for that: (1) in general more tar is released from biomass, (2) carbon conversion was very high and therefore the carbon content of the bed (important for tar cracking) developed only slowly.

Hydrogen Sulphide – H_2S concentrations of 200 – 800 ppm in the fuel gas were measured with German lignite as fuel. This corresponded to a release of 20 – 50% of the fuel sulphur. H_2S concentration reached a maximum at 850°C as the breakdown of organic sulphur components increased with temperature, while the higher temperatures also increased sulphur-ash reactions leading to increased sulphur retention. Pressure was found to reduce the extent of sulphur retention and the H_2S concentration in the fuel gas increased from 200 – 400 ppm to 400 – 800 ppm in the range of 1 – 20 bar. It was shown that steam increased the fuel-S to gas conversion as more fuel-S reacted with steam and H_2 to form H_2S . A linear relationship between the H_2S concentration in the fuel gas and the sulphur content of the fuel was found. For

example Daw Mill coal contains 1.6% sulphur and up to 2000 ppm of H_2S was measured in the fuel gas. In order to investigate the possibility of in-bed sulphur capture under oxy-fuel conditions, part of the silica sand was replaced with dolomite. With 60% dolomite/sand at 850°C , the H_2S content of the fuel gas could be reduced from 300 to 200 ppm. At 950°C under otherwise similar conditions, the H_2S content was reduced to 50 ppm. It was concluded that because of the high partial pressure of CO_2 in an oxy-fuel system, a higher temperature was necessary to calcine CaCO_3 effectively, than would be needed for an air blown gasifier.

Ammonia – NH_3 concentrations in the fuel gas between 500 and 2500 ppm were measured during oxy-fuel gasification of German lignite. A number of effects were found to affect the NH_3 concentration in the fuel gas using different gasification conditions and fuels: (1) steam increased the amount of NH_3 as more fuel-N is hydrogenated, (2) temperature and pressure affected the gas equilibrium of NH_3 , N_2 and H_2 , and (3) differences in carbon conversion as fuel-N is mostly in the carbon matrix and therefore only released if the carbon is converted.

- (10) **Thermodynamics:** The thermodynamic trends for the gas phase (water-gas shift reaction and steam reforming reaction) were calculated for the case of steam and CO_2 gasification. It was found that the equilibrium composition of the gas phase for steam gasification is more temperature dependent than for CO_2 gasification due to the higher H_2 content of the fuel gas. In a next step, the fuel gas composition from the laboratory scale reactor was compared with calculated equilibrium gas compositions. It was found that experimental measured levels of CH_4 could not be predicted by calculation as CH_4 is mainly a product of pyrolysis. Besides this, at 950°C good agreement between the experimental and theoretical values was found. At lower temperatures the fuel gas was found not to be in thermodynamic equilibrium. It was concluded that thermodynamic gas phase calculations can be used to predict the performance of an oxy-fuel fluidised bed gasifier if temperatures are as high as 950°C and the carbon conversion can be assumed to be 100% or is known. As mentioned before the amount of CH_4 in the fuel gas cannot be accurately predicted in this way.

- (11) **Summary - Feasibility of an oxy-fuel Spouted Bed Process:** The main objective of this study was to investigate the performance of an oxy-fuel fluidised bed process. The main findings regarding operability, carbon and energy conversions, fuel gas heating value and emissions have been summarised above. These data indicate that good gasification performance can be achieved in an oxy-fuel fluidised bed gasifier with low rank coals. It has also been shown that the performance of a gasifier using CO_2 as gasification agent, temperature moderator and fluidising agent is comparable to a gasifier using steam. As far as it can be assessed with the work carried out with the laboratory scale reactor in this study, it can be concluded that an oxy-fuel fluidised bed process is a feasible process option. However in a wider perspective, four key requirements need to be fulfilled before such a process can be developed to the next stage: (1) Requirement to capture the CO_2 produced by energy production from coal. Without carbon capture and storage, no pure stream of CO_2 would be available at the downstream end of the plant and the concept of CO_2 recycle would be not applicable (2) Entrained flow gasifiers have a significantly better performance with higher rank coals than fluidised bed gasifiers. Therefore for an oxy-fuel fluidised bed process to be attractive, it has to be based on a fuel not suitable for entrained flow systems. For example, coal very high in corrosive ash or sulphur and co-processing of biomass/waste with changing properties or high energy requirements for pulverisation. (3) O_2 /steam blown gasifiers are used since the original Winkler process was developed beginning of last century. A novel O_2/CO_2 gasifier in combination with CCS needs to have a significantly better efficiency, if integrated in an IGCC, for such a process to become feasible. The main advantages could be energy saving by using the pure, pressurised CO_2 from the CCS plant instead of having to produce steam and by using the entire process stream for power generation in the steam turbine. (4) The development of a gas turbine suitable for operation with a high partial pressure of CO_2 . In conclusion it can be said that as far as it can be judged from this project, oxy-fuel fluidised bed gasification process could be an option for coal based power generation in a CO_2 emission restricted future.

11.2 Recommendation for Future Work

11.2.1 Design Modification for the Spouted Bed Reactor

Based on the extensive experience with the spouted bed reactor under a wide range of conditions the following modifications are suggested to improve the performance and to extend the range of possible operating conditions:

- (1) Two operational problems at the base of the reactor were identified and changes to the design are suggested: (1) The dead zone around the spout and build up of agglomerated material was identified as an operational problem. To avoid the dead zone and to encourage the movement of particles at the conical shaped base, additional gas injection points on the slope of the cone could be used. A drawing of the proposed design is shown in Figure 77 (right). At the present scale of the reactor, a ring of 1 mm holes around the central spout are probably a realistic option. The fluidising gas would be split into two parts, one used to pneumatically inject the fuel into the reactor and the second one injected via these jets on the slope of the base cone. This would also allow preheating part of the gas without having to preheat the fuel. The conical base can be machined from a solid piece of stainless steel, with a hole in the middle for the spout line. (2) Agglomeration of particles in the spout due to preheating of the injection line. Fuel agglomeration was found to occur always at the very top of the spout line, which is presumably the hottest point. A design modification is suggested in Figure 77 (centre), where an additional gas inlet is added just below the top of the spout. This could be used to inject steam and reduce the temperature in this area.
- (2) It would be desirable to collect entrained particles and condensable products (water and tar) separately and to collect the condensable products from the start up phase separately from the ones produced during steady state. A suggested modification would be to replace the counter weight with a porous disc. The disc would be placed on top of the glass liner and a thermocouple would go through a tight central hole in the middle of the disc. This would retain entrained particles in the reactor and allow tar and water to pass through as the temperature of the disc would be far higher than the boiling point of these compounds. After the reactor, a T-piece splits the gas line in two, leading to two separate tar traps, one for use during start up and one for steady

state operation. The tar traps are joined at the top with a three way valve. This way the use of high temperature valves can be avoided and both tar traps are always at reactor pressure, allowing switching between them without causing pressure fluctuations.

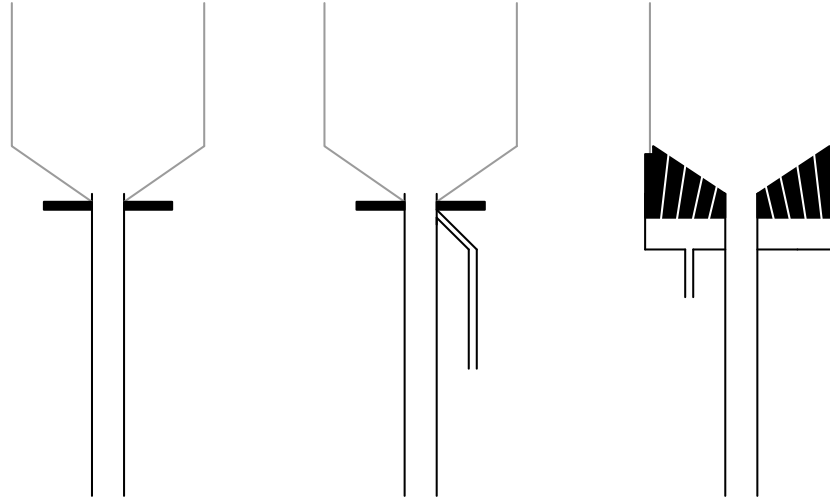


Figure 77: Three spout configurations: left – current configuration used in this project, middle – proposed configuration to optimise steam injection, right – proposed configuration to improve bed mixing

11.2.2 Possible Further Work

This study proved that the fluidised bed reactor produces repeatable results over a wide range of conditions. It further showed that oxy-fuel gasification could be a promising way to use a range of fuels for clean power generation. Based on this work a number of studies are suggested to further investigate the potential of the concept.

- (1) The use of sand and the associated problem with sand-ash agglomeration was shown to prevent the use of high temperatures and high oxygen levels. Using limestone as bed material and German lignite as fuel, it should be theoretically possible to vary the O/C value over a wide range. This would allow a systematic investigation of the influence of O/C ratios at high temperatures. In addition it would be possible this way to heat the bed above 1000°C by a combination of external heating and heat generated from combustion. For future large scale applications, the maximum operating temperature is a key factor.
- (2) As mentioned in the discussion, unlike H_2S , NH_3 is not the main nitrogen compound in the fuel gas. To investigate the nitrogen release in more detail, it would be

interesting to firstly, measure the concentration of HCN in the fuel gas and secondly, to calculate the equilibrium concentrations of HCN, NH_3 and N_2 under the specific conditions used. This would provide a better insight into the processes involved and the results could be compared to work carried out previously at Imperial College related to the nitrogen release under air blown conditions.

- (3) In this project the fuel gas was analysed for CO, CO_2 , H_2 , CH_4 , H_2S and NH_3 . A gas sample could be metered with a dry gas meter into a gas bag and the fuel gas analysed in a GC to identify further compounds, if any. Most likely, the fuel gas contains a small quantity of compounds with a boiling point below room temperature, especially at lower gasification temperature or with biomass as fuel.
- (4) The behaviour of the inorganic fuel material under different gasification conditions could be investigated by calculating the phase diagram (Calphad method; Example: FactSage software package). This work could help to understand and predict the problems with operability identified in this study. It also could help to identify if the high partial pressure of CO_2 can cause these problems. The phase diagram would give an indication at which temperature the inorganic materials in the process are in which phase and therefore could give, for example, an indication on why some fuels tend to block the spout line.
- (5) The data obtained in the project could be used to derive kinetic data for the oxy-fuel gasification process. A kinetic model could be further used to develop a model of the gasifier and assist in further work to scale up the process.
- (6) The findings in the project could be used to develop a model of an IGCC oxy-fuel plant. A relatively simple gasification model could be developed based on the fact that at high gasification temperatures the fuel gas is in thermodynamic equilibrium. A plant model should include all key parts of an IGCC and would provide a useful insight into the overall efficiency. It would be especially interesting to compare O_2/CO_2 gasification with O_2 /steam gasification on a plant wide scale to discuss the potential increase in efficiency by using the recycled stream of CO_2 instead of having to raise the steam with process heat. The energy penalty introduced by the ASU could

also be investigated in more detail by comparing the process to an air blown configuration.

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Appendix

A. Calibrations

A.1 Dry Gas Meter

The dry gas meter was calibrated using a bubble column to measure the actual flow of CO₂ from a mass flow controller. The calibrations and the formula used to correct the dry gas meter reading are shown in Figure 78.

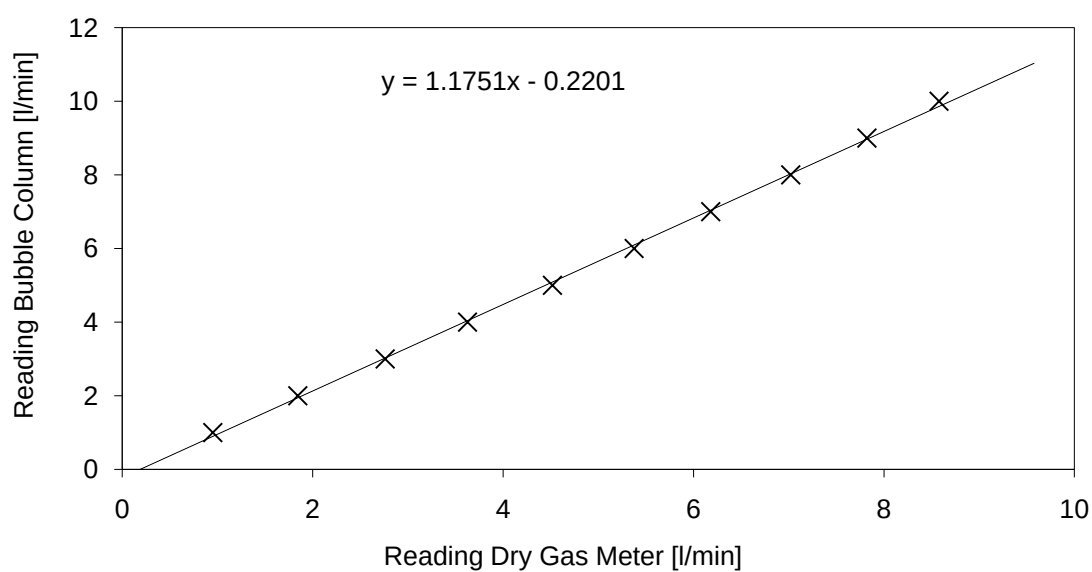


Figure 78: Calibration of the dry gas meter using a bubble column.

A.2 Hydrogen Analyser

The hydrogen analyser used in this project was calibrated to measure H_2 in CO_2 . In order to estimate the H_2 content of the fuel gas for experiments with nitrogen in the fuel gas, a calibration curve for the hydrogen analyser was taken. Different mixtures of H_2 in N_2 were produced using mass flow controller. The calibration curve and the correction factor are shown in Figure 79.

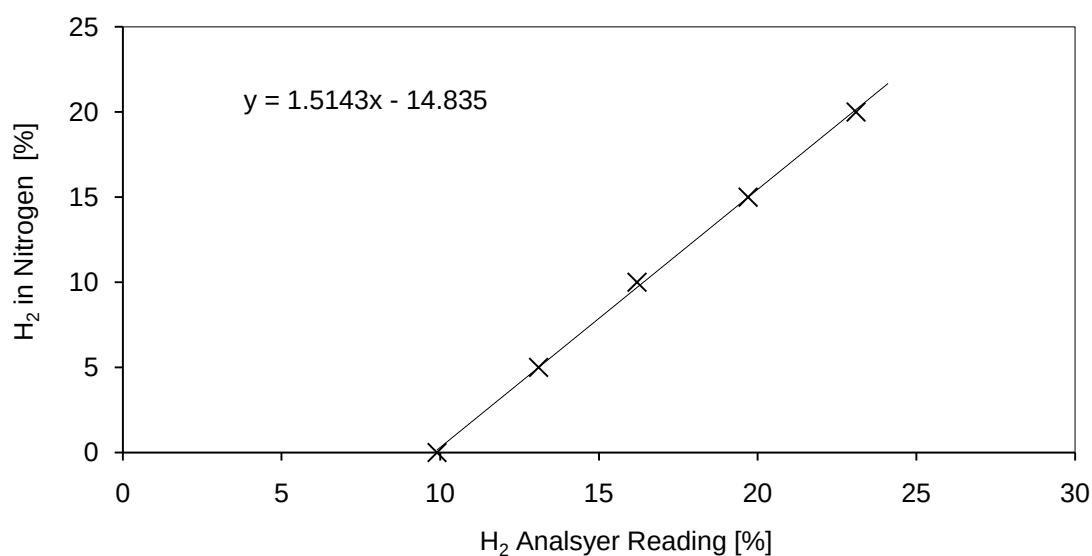


Figure 79: Calibration curve to estimate hydrogen content in fuel gases containing nitrogen.

A.3 Ammonia Analysis

The calibration data for the ion selective electrode for each set of experiment is shown in Table 19. The measured signal strength and the calculated ammonia concentration for each measurement are listed in Table 20.

Table 19: Calibration data for the ammonia measurement

Test number and measurement of calibration solution [mV]													
[ppm]	62/63	64	65	67-69	76-78	80/81	83/84/87/88	100/109-111	112-115	120-123	124-128	130/131/133-137	139/140/143
100	147.1	143.2	133.8	136.4	127.6	125	134.8	151.1	125.8	121.2	124.1	108.6	102.7
1000	202.1	199.6	190.2	195.4	184.9	181.7	186.7	176.4	180.4	174.8	176	160.3	153.9
10000	251.4	251.3	242.9	247.7	247.7	235.2	237.1	226.3	230.3	224	226.6	208.4	203.6

Table 20: Ammonia measurement: test number, mV signal and calculated ammonia concentrations

#	61	62	63	64	65	67	68	69	76	77	78	80	81	83	84
[mV]	90	99.3	150.5	143.2	143.7	157.2	145.4	153.8	130.6	139.6	123.4	189.1	129	231.4	218.7
[ppm]	136	12	112	97	148	225	138	196	116	164	88	1430	116	7627	4307
#	87	88	100	109	110	111	112	13	115	115	120	121	122	123	124
[mV]	235.6	229.3	229	232.4	231.9	230.1	231.4	236.9	242.1	212.8	136.6	174.6	135	120.2	209.4
[ppm]	9213	6939	13733	16789	16301	14656	10034	12781	16067	4426	194	1064	180	93	4547
#	125	126	127	128	130	131	133	134	135	136	137	139	140	143	
[mV]	128.4	137.6	213.6	209.6	211.6	145.4	211.4	202.4	202	184.4	203.4	204.2	209.4	205.8	
[ppm]	120	181	5491	4588	11205	530	11102	7332	7198	3198	7678	7966	10124	8576	

B. High Pressure Fluidised Bed Reactor

B.1 High Pressure Safety Calculations

The reactor body is made from Incoloy Alloy 800HT. This alloy has a high creep resistance combined with a resistance to high temperature corrosion that made it the material of choice. The chemical composition is given in Table 21. In the beginning of the project a new reactor shell was machined and the shell was replace after 50 experiments.

Table 21: Chemical composition of Incoloy Alloy 800HT [162]

Element	wgt[%]
Ni	30 - 35
Cr	19 - 23
Fe	39.5
C	0.06 - 0.1
Mn	1.5
S	0.015
Si	1.0
Cu	0.75
Al	0.15 - 0.6
Ti	0.15 - 0.6

A safety calculation was carried out at the beginning of the project to confirm that the reactor can be operated at 30 bar_g and 1000°C in a safe manner. Data for creep strength [163] were plotted against temperature and extrapolated to obtain the value for 1000°C (Figure 81). The calculation (Equation 17) to obtain the minimum wall thickness for a given internal diameter of pipe, temperature and pressure was taken from the *High Pressure Safety Code* [164] and *BS 5500* [165]. Figure 80 shows the minimum wall thickness required for operating the reactor at 1000°C for 1000 hours. The wall thickness of the reactor shell is 7 mm while a design pressure of 30 bar_g requires 6 mm wall thickness according to Equation 17. It can be concluded that is safe to operate the reactor at 30 bar_g and 1000°C.

$$e = \frac{pd_i}{2f - p}$$

e: minimum wall thickness

p: design pressure

f: creep strength (for 1000 hours at given temperature)

d_i: internal diameter

Equation 17

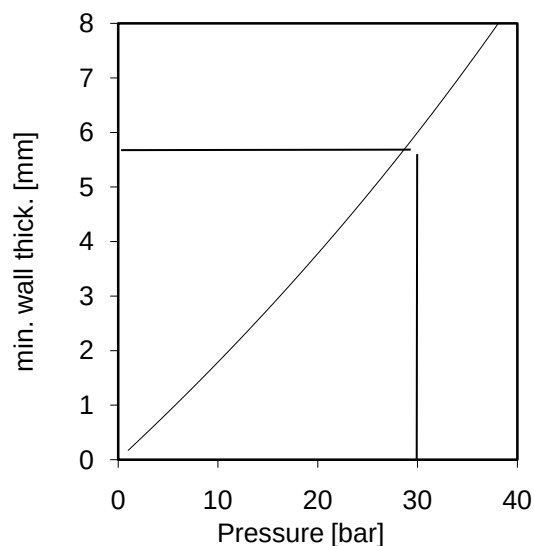


Figure 80: Required minimum wall thickness for design pressure up to 40 bar_g at 1000°C and for 1000 hours.

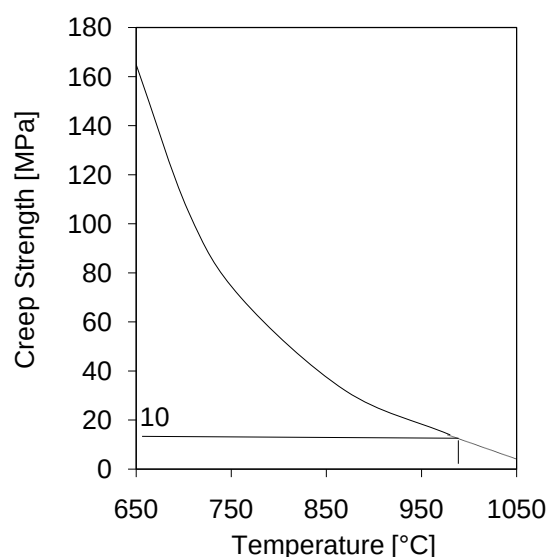


Figure 81: Creep Strength of Incoloy Alloy 800HT at elevated temperature [163]. Extrapolated to 1000 hours.

B.2 Resistance heater

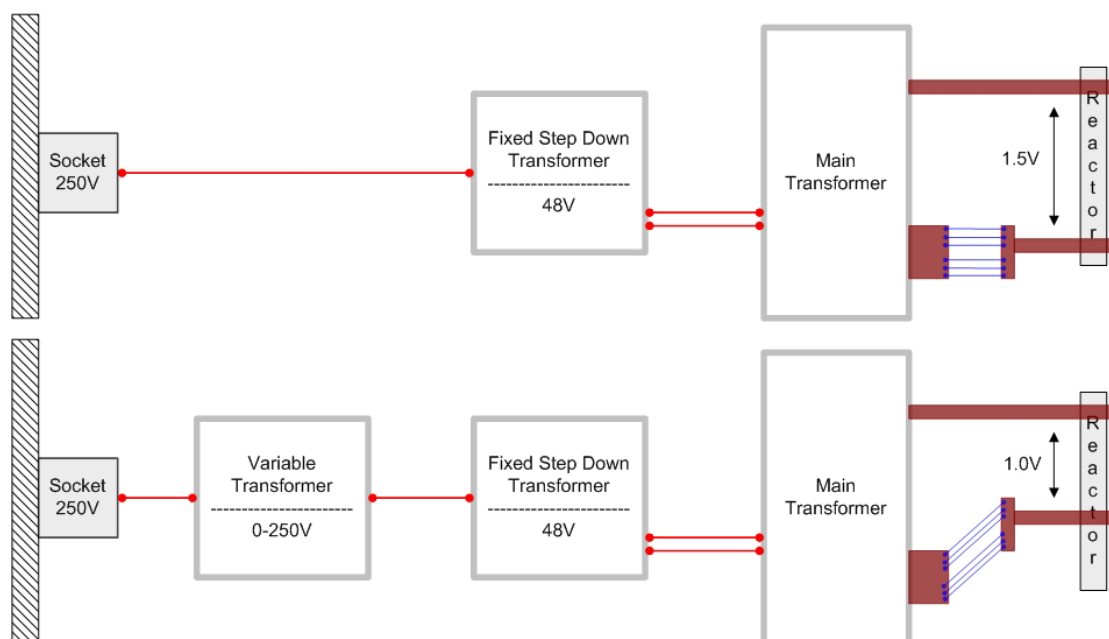


Figure 82: Top: old set up of resistance heater; Bottom: new set up with variable transformer and raised bottom electrode.

C. Equations

C.1 Minimum Fluidising Velocity

The minimum fluidising velocity (U_{mf}) was calculated with the formula below [17] :

$$\frac{1.75}{\varepsilon_{mf}^3 \phi_s} \left(\frac{d_p U_{mf} \rho_g}{\mu} \right)^2 + \frac{150(1 - \varepsilon_{mf})}{\varepsilon_{mf}^3 \phi_s^2} \left(\frac{d_p U_{mf} \rho_g}{\mu} \right) = \frac{d_p \rho_g (\rho_s - \rho_g) g}{\mu^2} \quad \text{Equation 18}$$

d_p	: particle diameter [m]
ε_{mf}	: void fraction
ϕ_s	: sphericity
ρ_g	: gas density [kg/m ³]
ρ_s	: solid density [kg/m ³]
μ	: viscosity [kg/ms]
g	: gravity [9.81 m/s ²]

C.2 Error Calculation

The linear error propagation was calculated based on the equation below:

$$\begin{aligned} \Delta X = & \left| 53.57 \frac{(X_{CO_2} + X_{CH_4})F}{FFR \cdot X_{C-coal}} \right| \Delta X_{CO} + \left| 53.57 \frac{(X_{CO} + X_{CH_4})F}{FFR \cdot X_{C-coal}} \right| \Delta X_{CO_2} \\ & + \left| 53.57 \frac{(X_{CO_2} + X_{CO})F}{FFR \cdot X_{C-coal}} \right| \Delta X_{CH_4} + \left| 53.57 \frac{1}{FFR \cdot X_{C-coal}} \Delta F_{CO_2} \right| + \\ & \left| 53.57 \frac{(X_{CO} + X_{CO_2} + X_{CH_4})F - F_{CO_2}}{FFR^2 \cdot X_{C-coal}} \Delta FFR \right| + \left| 53.57 \frac{(X_{CO} + X_{CO_2} + X_{CH_4})}{FFR \cdot X_{C-coal}} \Delta F \right| \end{aligned}$$

Equation 19

D. Thermodynamic Calculations

D.1 Major Gas Phase Constituents

The equilibrium model used by Watkinson et al. [138] to predict the fuel gas composition for a 50 kg coal/h air-blown spouted bed gasifier was adopted for the lab scale oxy-fuel spouted bed gasifier used in this project. The model incorporates elementary mass balance equations for C, H, and O, the equilibrium constants for water-gas shift reaction and methanation reaction, and Dalton's Law. The following assumptions are made:

- Fuel gas concentration is determined solely by stoichiometric and thermodynamic constraints.
- Carbon conversion X is given from experimental data.
- The fuel gas only contains CO_2 , CO , H_2 , H_2O , and CH_4 .
- The fuel gas is in water-gas shift and methanation equilibrium, at gasifier temperature and pressure.
- All gases are treated as ideal gases [7].
- All free oxygen is consumed under these conditions [134].
- All hydrogen in the feedstock is released either as H_2 , steam or CH_4 .
- Steam in the fuel gas is produced by the moisture content of the feedstock.

The input flow rates (n_i) for H_2 , Steam, CO_2 , O_2 and C for a specific gasification experiment are known, carbon conversion X is calculated from the experimental results and the equilibrium constants can be calculated knowing average bed temperature and pressure. The resulting system of non linear equations is solved for y_{CO} , y_{CO_2} , y_{H_2} , y_{CH_4} , $y_{\text{H}_2\text{O}}$ and n (total number of moles) using the experimental values for the gas composition as initial guess.

List of equations:

Dalton's Law:

$$yCO + yCO_2 + yH_2 + yH_2O + yCH_4 = 1 \quad \text{Equation 20}$$

Elementary Balance for H₂:

$$(yH_2 + yH_2O + 2yCH_4)n - nH_2 - nH_2O = 0 \quad \text{Equation 21}$$

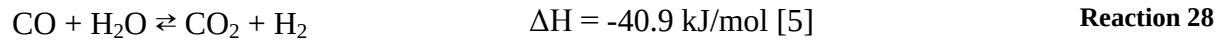
Elementary Balance for O₂:

$$(yCO/2 + yCO_2 + yH_2O/2)n - nCO_2 - nH_2O/2 - nO_2 = 0 \quad \text{Equation 22}$$

Elementary Balance for C:

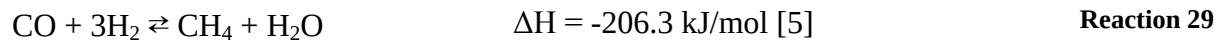
$$(yCO + yCO_2 + yCH_4)n - nCO_2 - nC * X = 0 \quad \text{Equation 23}$$

Water-gas Shift Reaction:



$$\frac{(yH_2)(yCO_2)}{(yCO)(yH_2O)} = 0.0265 \exp(3956/T_b) [166] \quad \text{Equation 24}$$

Steam Reforming Reaction:



$$\frac{(yCH_4)(yH_2O)}{(yCO)(yH_2)^3 p^2} = 6.538 \times 10^{-18} \exp(27020/T) [167] \quad \text{Equation 25}$$

D.2 Sulphur Capture Equilibrium

Sulphur Capture (data taken from Diego et al. [168])

Direct sulfidation:



$$\frac{(P_{\text{H}_2\text{O}} P_{\text{CO}_2})}{P_{\text{H}_2\text{S}}} = 4.66 \times 10^{12} \exp(13212/T) \quad \text{Equation 26}$$

Indirect sulfidation:



$$P_{\text{CO}_2} = 4.14 \times 10^{12} \exp(-20474/T) \quad \text{Equation 27}$$



$$\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{S}}} = 1.13 \exp(7262/T) \quad \text{Equation 28}$$

E. Experimental Data

I - Fuel: German Lignite, Oxy-Fuel														
Gasification Conditions					Fuel Gas Composition (dry)						Gasification Performance			
T [°C]	P [bar]	FFR [g/min]	F _{in} [l/min]	Steam/O ₂ /CO ₂ [%]	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	NH ₃ [ppm]	H ₂ S [ppm]	X [%]	F _{out} [l/min]	LHV [MJ/m ³]	E _{conv} [%]
750	1	1.74	1.76	0/0/100	24.2	62.9	10.6	2.3			33	2.72	5.1	31
750	1	1.83	2.64	0/0/100	23.3	65.9	9.0	1.8	836	300	38	3.79	4.6	37
750	1	1.71	2	0/0/100	23.0	64.1	10.5	2.4	809	600	35	3.02	5.0	34
750	1	1.71	1.76	0/5/95	25.5	61.7	10.8	2.1			39	2.73	5.2	32
750	1	1.76	1.76	0/10/90	28.1	58.2	11.3	2.4			45	2.82	5.7	36
850	1	1.03	2	0/0/100	41.0	45.9	11.7	1.4			90	3.45	7.0	91
850	1	1.64	1.76	0/0/100	45.1	37.4	15.4	2.1			61	3.43	8.2	66
850	1	1.71	2.64	0/0/100	44.7	39.4	14.1	1.8	1640	300	74	4.75	7.9	85
850	1	1.74	1.76	0/5/95	44.6	37.8	15.5	2.0			62	3.43	8.1	62
850	1	1.69	3	0/5.5/94.5	44.6	38.8	14.9	1.7	2592		93	5.42	7.9	99
850	1	1.77	1.76	0/10/90	49.7	30.7	17.4	2.2			68	3.56	9.0	71
850	1	1.69	1.76	0/10/90	45.0	35.0	18.0	2.1			65	3.45	8.5	67
850	1	1.69	1.76	0/10/90	44.1	36.2	17.6	2.1			70	3.54	8.3	68
850	1	1.62	1.76	0/10/90	44.2	37.3	16.7	1.9			72	3.47	8.1	68
850	1	1.64	1.76	0/20/80	41.1	39.1	17.6	2.2			77	3.45	8.0	65
850	1	1.85	1.76	0/10/90	42.3	39.4	16.2	2.1			63	3.47	7.9	58
850	1	1.77	1.76	0/10/90	45.3	35.4	17.3	2.0			69	3.59	8.4	66
850	1	1.76	1.76	0/10/90	45.1	35.3	17.5	2.2			70	3.61	8.4	67
850	1	1.56	1.76	0/10/90	46.1	35.3	16.9	1.8	2335	400	81	3.6	8.3	75
850	1	1.58	1.76	0/10/90	47.4	34.2	16.6	1.8		400	80	3.61	8.5	75
850	1	1.63	1.76	0/10/90	47.0	34.6	16.5	1.8	1193	400	78	3.61	8.4	73
850	1	1.61	1.76	0/10/90	40.0	43.3	14.9	1.8	2036	500	68	3.31	7.4	59
850	1	1.71	1.76	0/10/90	40.7	41.2	15.9	2.2		400	67	3.44	7.7	61
850	1	1.60	1.76	0/10/90	44.3	37.7	16.2	1.8	1937	400	73	3.46	8.1	68

II - Fuel: German Lignite, Oxy-Fuel														
Gasification Conditions					Fuel Gas Composition (dry)						Gasification Performance			
T [°C]	P [bar]	FFR [g/min]	F _{in} [l/min]	Steam/O ₂ /CO ₂ [%]	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	NH ₃ [ppm]	H ₂ S [ppm]	X [%]	F _{out} [l/min]	LHV [MJ/m ³]	E _{conv} [%]
850	1	1.64	1.76	0/10/90	46.0	35.5	16.5	1.9	1677	400	74	3.53	8.4	70
850	1	1.68	1.76	0/10/90	49.6	31.5	17.0	1.9		400	77	3.67	8.9	75
850	1	1.88	1.76	0/10/90	48.1	32.6	17.4	1.9		400	70	3.71	8.7	67
850	1	1.88	1.76	0/10/90	47.5	33.1	17.7	1.7		300	70	3.71	8.6	66
850	1	1.77	1.76	0/10/90	47.8	32.7	17.7	1.9	2481	300	73	3.69	8.7	70
850	1	1.74	1.78	0/10/90	43.2	37.0	17.8	2.0	2263	300	67	3.55	8.2	65
950	1	1.76	1.76	0/0/100	57.6	21.8	18.9	1.7			88	4.3	10.0	95
950	1	1.85	1.76	0/10/90	49.4	30.0	18.4	2.1			75	3.87	9.1	74
950	1	1.82	1.76	0/5/95	51.0	29.4	17.6	2.0			73	3.86	9.1	75
950	1	1.71	2.64	0/0/100	50.7	33.5	14.1	1.7	1140	300	87	5.02	8.6	98
950	1	2.28	2.64	0/0/100	53.7	26.1	18.3	1.9		400	80	5.76	9.5	93
850	5	1.39	4	0/3.7/96.3	29.2	63.1	6.6	1.1			76	5.4	4.8	73
950	5	1.32	4	0/3.7/96.3	40.9	49.9	8.0	1.2	883	500	94	5.7	6.5	109
850	5	1.34	4	0/3.7/96.3	34.8	56.7	7.4	1.1	5023		92	5.65	5.6	92
850	5	1.44	4	0/3.7/96.3	30.9	61.3	6.7	1.1	1432		78	5.48	5.1	75
850	5	6.24	5	0/9/91	37.2	42.5	16.1	4.3		700	44	9.4	8.1	48
850	5	1.35	5	0/3/97	29.0	64.8	5.4	0.8	1215		89	6.55	4.6	87
850	5	1.25	6	0/2.5/97.5	26.4	68.7	4.3	0.6	863		99	7.55	4.0	95
850	5	1.25	7	0/1.8/98.2	23.6	71.9	3.9	0.6	1161		98	8.56	3.6	97
850	5	3.00	8	0/3.7/96.3	30.5	61.0	7.2	1.3		300	74	11	5.1	73
850	10	2.77	8	0/0/100	21.0	72.4	4.8	1.8			55	10.3	3.9	56
950	10	3.06	8	0/3.7/96.3	39.9	50.5	8.1	1.4	1376	500	98	13.8	6.5	113
850	10	2.80	8	0/10/90	21.0	72.7	4.8	1.5			82	10.3	3.8	54
850	10	2.78	8	0/3.7/96.3	25.8	67.0	5.7	1.4			69	10.5	4.5	65
850	10	2.81	8	0/0/100	27.5	65.5	5.7	1.3			68	10.8	4.6	69
850	10	2.95	9	0/3.3/96.7	30.7	61.9	6.2	1.2	1735		88	12.4	5.0	82
850	10	3.05	10	0/3/97	23.8	70.4	4.8	1.1	1605		74	12.87	3.9	65
850	10	2.87	11	0/2.8/97.2	27.6	66.4	5.1	0.9			92	14.4	4.4	86

II - Fuel: German Lignite, Oxy-Fuel														
Gasification Conditions					Fuel Gas Composition (dry)						Gasification Performance			
T [°C]	P [bar]	FFR [g/min]	F _{in} [l/min]	Steam/O ₂ /CO ₂ [%]	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	NH ₃ [ppm]	H ₂ S [ppm]	X [%]	F _{out} [l/min]	LHV [MJ/m ³]	E _{conv} [%]
850	15	3.66	12	0/3.7/96.3	22.6	70.8	5.2	1.3		300	72	15.4	3.9	64
850	15	5.34	12	0/3.7/96.3	23.7	68.7	5.9	1.7		400	56	15.99	4.3	50
850	15	4.55	12	0/3.7/96.3	19.0	75.0	4.6	1.4			54	15.09	3.5	44
850	15	4.31	12	0/3.7/96.3	24.1	68.1	6.2	1.5		400	66	15.85	4.3	62
850	20	6.29	16	0/3.7/96.3	19.2	73.0	5.6	2.2			54	20.65	3.9	50

IV - Fuel: German Lignite, Oxy-Fuel + Steam														
Gasification Conditions					Fuel Gas Composition (dry)						Gasification Performance			
T [°C]	P [bar]	FFR [g/min]	F _{in} [l/min]	Steam/O ₂ /CO ₂ [%]	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	NH ₃ [ppm]	H ₂ S [ppm]	X [%]	F _{out} [l/min]	LHV [MJ/m ³]	E _{conv} [%]
750	1	1.61	2.62	0/24/76	21.7	60.0	15.9	2.5		700	45	3.40	5.4	45
850	1	1.73	2.40	7/26/67	37.4	37.6	22.8	2.1	2735	600	74	3.95	8.0	71
850	1	1.74	2.62	0/24/76	39.3	37.3	21.3	2.0		500	84	4.65	8.1	84
850	1	1.71	2.64	0/47/53	34.4	34.7	28.6	2.3	2223	600	86	4.30	8.3	82
850	1	1.67	2.67	0/70/30	29.3	30.7	37.2	2.7	1447		87	3.92	8.8	80
950	1	1.70	2.62	0/24/76	44.3	32.9	20.8	2.0	2236	500	85	4.60	8.6	90
950	1	1.70	2.64	0/47/53	37.9	31.2	28.5	2.4	680	500	84	4.25	8.8	86
850	5	1.31	4.02	4/15/81	32.8	55.6	10.1	1.5	1501	500	84	5.01	5.8	86
850	5	1.39	4.04	4/31/65	29.3	53.4	15.4	1.9	914	700	81	4.67	6.1	80
850	10	3.09	8.04	4/15/81	30.3	57.0	10.7	2.1	932	700	84	10.63	5.8	77
850	15	4.51	11.97	4/16/80	24.7	61.6	10.4	3.3	948	700	74	15.30	5.5	73
750	1	1.61	2.62	0/24/76	21.7	60.0	15.9	2.5		700	45	3.40	5.4	45

V - Fuel: German Lignite, Sand/Dolomite mixtures as bed material, all experiments with Steam/O₂/CO₂ = 0/10/90														
Gasification Conditions					Fuel Gas Composition (dry)						Gasification Performance			
T [°C]	P [bar]	FFR [g/min]	F _{in} [l/min]	Sand/Dolomite [%]	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	NH ₃ [ppm]	H ₂ S [ppm]	X [%]	F _{out} [l/min]	LHV [MJ/m ³]	E _{conv} [%]
850	1	1.76	1.76	10/90	42.8	39.0	16.2	2.0		300	67	3.45	7.9	62
850	1	1.73	1.76	10/90	50.0	29.8	18.2	2.1		200	74	3.70	9.1	75
850	1	1.42	1.76	10/90	56.9	22.5	19.0	1.5	1189	200	91	3.75	9.8	100
850	1	1.50	1.76	10/90	58.0	20.5	19.8	1.6	1426	200	95	3.96	10.1	104
960	1	1.48	1.76	10/90	60.8	20.8	16.5	1.9	1189	50	98	3.85	10.2	103

VI - Fuel: German Lignite, Pyrolysis and Partial Oxidation														
Gasification Conditions					Fuel Gas Composition (dry)						Gasification Performance			
T [°C]	P [bar]	FFR [g/min]	F _{in} [l/min]	O ₂ /N ₂ [%]	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	NH ₃ [ppm]	H ₂ S [ppm]	X [%]	F _{out} [l/min]	LHV [MJ/m ³]	E _{conv} [%]
750	1	1.79	1.76	0/100	7.8	5.5	19.4	3.0				3.11		
850	1	1.67	1.76	0/100	12.2	2.5	20.3	2.8				2.97		
850	1	1.62	1.76	0/100	11.7	3.6	20.0	2.4		150		3.42		
950	1	1.74	1.76	0/100	18.0	0.7	29.0	1.8				4.10		
850	5	1.33	4	0/100	6.1	0.6	10.0	1.5				5.28		
850	10	3.03	8	0/100	5.4	2.0	10.6	1.9				10.80		
850	15	5.29	12	0/100	5.5	2.6	10.2	2.1				17.07		
850	15	3.99	12	0/100	5.6	2.4	8.5	3.1				16.01		
850	20	5.10	15	0/100	6.0	1.6	10.0	2.3				18.65		
850	1	1.72	1.76	10/90	17.3	6.7	23.0	2.6	2142	200	41	3.16	5.7	41
950	1	1.77	1.76	10/90	25.0	2.2	28.0	2.0	296	50	53	3.73	7.0	57

VII- Fuel: Daw Mill Coal														
Gasification Conditions					Fuel Gas Composition (dry)						Gasification Performance			
T [°C]	P [bar]	FFR [g/min]	F _{in} [l/min]	O ₂ /CO ₂ [%]	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	NH ₃ [ppm]	H ₂ S [ppm]	X [%]	F _{out} [l/min]	LHV [MJ/m ³]	E _{conv} [%]
850	1	2.88	2	10/90	16.7	68.3	11.6	3.4	1436	1900	15	2.79	4.7	16
850	1	1.90	2	10/90	13.7	73.0	10.0	3.3	1889	1500	21	2.66	4.1	20
850	1	1.45	2	10/90	13.0	76.4	7.9	2.6	828	1500	24	2.51	3.5	21
900	1	1.80	2	5/95	11.3	78.5	7.9	2.4			23	2.70	3.2	
950	1	1.48	2	10/90	19.9	66.7	10.7	2.7	842	1500	36	2.87	4.7	31

VIII - Fuel: Polish Coal														
Gasification Conditions					Fuel Gas Composition (dry)						Gasification Performance			
T [°C]	P [bar]	FFR [g/min]	F _{in} [l/min]	Stream/O ₂ /CO ₂ [%]	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	NH ₃ [ppm]	H ₂ S [ppm]	X [%]	F _{out} [l/min]	LHV [MJ/m ³]	E _{conv} [%]
850	1	2.80	2.64	0/0/100	11.8	76.8	8.1	3.3	4142	500	15	3.32	3.7	14
950	1	1.74	2.64	0/0/100	26.9	63.0	8.0	2.2	4461	200	27	3.67	5.1	35
950	1	1.72	2.64	23/0/77	30.2	51.9	15.2	2.6	4352	400	37	3.50	6.5	43

IX- Fuel: CO-Gasification of Olive Bagasse (OB) and German Lignite (GL)														
Gasification Conditions					Fuel Gas Composition (dry)						Gasification Performance			
T [°C]	OB/GL [%]	FFR [g/min]	F _{in} [l/min]	O ₂ /CO ₂ [%]	CO [%]	CO ₂ [%]	H ₂ [%]	CH ₄ [%]	NH ₃ [ppm]	H ₂ S [ppm]	X [%]	F _{out} [l/min]	LHV [MJ/m ³]	E _{conv} [%]
850	20/80	1.56	2.64	0/100	41.2	44.4	12.6	1.8	2724	200	84	4.40	7.3	85
850	30/70	1.50	2.64	0/100	41.6	44.8	11.8	1.8	2634	200	102	4.39	7.2	90
850	40/60	1.49	2.64	0/100	39.3	48.1	10.8	1.8	2638	150	100	4.45	6.8	90
850	50/50	1.54	2.64	0/100	37.8	49.1	11.1	2.0	2724	150	99	4.45	6.7	89
850	10/90	1.58	1.76	10/90	46.7	35.5	15.9	1.9			78	3.38	8.4	72
850	20/80	1.58	1.76	10/90	45.1	35.5	17.3	2.2			86	3.42	8.4	76

F. Publications, Conferences and Planned Publications

Publications

- Spiegl, N., Sivena, A., Lorente, E., Paterson, N., Millan, M. , *Investigation of the Oxy-fuel Gasification of Coal in a Laboratory-Scale Spouted-Bed Reactor: Reactor Modifications and Initial Results*, Energy Fuels **2010**, 24, 5281–5288
- Spiegl N., Paterson, N., Millan, M., Kandiyoti, R., *Performance of a Fluidised Bed Gasifier under Oxy-Fuel Conditions*, 4th Conference on Clean Coal Technology Dresden, 2009

Planned Publications

- Performance of an Oxy-Fuel Fluidised Bed Gasifier under Atmospheric Pressure.
- Pressurised Oxy-Fuel Gasification of Lignite – Comparison Of Fluidised Bed Performance and Wire Mesh Reactor Measurements.
- H₂S and NH₃ Emissions from an Oxy-Fuel Fluidised Bed Gasifier.
- Thermodynamic Modelling of an Oxy-Fuel Fluidised Bed Gasifier.

Conferences and Workshops

- Young Scientists Round Table, Virtuhcon
Freiberg, Germany, 16 – 20/6/2008, oral presentation
- 7th European Conference on Coal Research & its Applications
Cardiff, UK, 3 – 5/09/2008, oral presentation
- British Carbon Group Spring Meeting
Manchester, UK, 31/03 – 1/04/2009, oral presentation
- 4th International Conference on Clean Coal Technology
Dresden, Germany, 18 – 21/5/2009, oral presentations
- 8th European Conference on Coal Research & its Applications
Cardiff, UK, 6 – 8/09/2010, oral presentations (2 papers accepted)
- 27th Annual International Pittsburgh Coal Conference
Istanbul, Turkey, 11 – 14/10/2010, oral presentation